UNIVERSITY
OF MICHIGAN
JUL 1 1953
PHYSICS
LIBRARY

REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XXXVII] *SECTION A* [NO. 4

APRIL 1953

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY C. VASUDEVA RAO,
SUPERINTENDENT (I/C), AND PUBLISHED BY THE INDIAN ACADEMY OF
SCIENCES, BANGALORE.

IST DAS DIRACSCHE VERFAHREN DER LINEARISATION NOTWENDIG?

V. S. VRKLJAN IN ZAGREB

Received March 27, 1951

BEKANNTLICH liefert das Diracsche Verfahren der Linearisation des Ausdrucks[1]

$$p_x^2 + p_y^2 + p_z^2 + m_0^2c^2 = \frac{u^2}{c^2}$$

hinreichende Bedingung dafür, um das Spinphänomen als auch das damit zusammenhängende magnetische Moment des Elektrons (bzw. des Positrons) theoretisch zu beherschen.* Es drängt sich aber die Frage auf, ob dieses *Dirac*sche Verfahren die einzige Möglichkeit der Linearisation bedeutet, dass es also nicht nur hinreichend, sondern auch notwendig ist, oder ob auch andere davon etwas verschiedene Möglichkeiten der Linearisation bestehen, welche ebenso zu den brauchbaren Gleichungen für das Elektron bzw. das Positron führen.†

I

Wir können leicht quadratische hermitische Matrizen 4. Ordnung finden, wo

$$(\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 m_0 c)\,(\beta_1 p_x + \beta_2 p_y + \beta_3 p_x + \beta_4 m_0 c) = a \,.\, 1 \,.\, \frac{u}{c} \,.\, b \,.\, 1 \,.\, \frac{u}{c} \tag{1}$$

wird; man braucht nur aus den *Dirac*schen Matrizen γ_r $(r = 1, 2, 3, 4)$ die neuen Matrizen

$$\alpha_r = a\gamma_r \text{ und } \beta_r = b\gamma_r \tag{2}$$

unter der Bedingung

$$a \,.\, b = 1 \tag{3}$$

definieren. Es erfüllen dann die Matrizen α_r und β_r die Bedingungen

$$\alpha_k\beta_l + \beta_l\alpha_k = 2\delta_{kl} \,.\, 1 \tag{4}$$

wo

$$\delta_{kl} = \begin{cases} 1 \; (k = 1 = 1, 2, 3, 4) \\ 0 \; (k = 1) \end{cases} \tag{5}$$

* Die obige Gleichung lässt sich bekanntermassen leicht verallgemeinern für den Fall, dass ein elektromagnetisches Feld vorhanden ist.

† Eine solche Frage scheint nicht nur vom rein erkenntnistheoretischen Interesse sein; sie könnte vielleicht auch vom physikalischen Standpunkt Interesse erwecken, da man von vornherein nicht sagen kann, zu welchen physikalischen Schlüssen die Antwort auf diese Frage führen könnte.

das bekannte Symbol von *Kronecker*[2] bedeutet. Die Bedingung (3) kann man indessen leicht durch geeignete Wahl der Grössen a und b erfüllen, z. B. $a = \sqrt{n+1} + \sqrt{n}$, $b = \sqrt{n+1} - \sqrt{n}$, wo n eine beliebige reelle Zahl bedeutet (dabei vor $\sqrt{n+1}$ in a und b dasselbe Vorzeichen gedacht).

Selbstverständlich erfüllen dann die Matrizen α_ν an und für sich als auch die Matrizen β_ν an und für sich nur die *Diracs*chen Regeln über die Antikommutativität, nicht aber die *Diracs*che Vorschrift, dass das Quadrat jeder dieser Matrix eine Einheitsmatrix ist.

Eine solche Interpretation führt jedoch zuletzt zurück zu der *Diracs*chen Theorie; denn man braucht nur die gewonnenen linearisierten Gleichungen mit dem Faktor vor $\frac{u}{c}$, also mit dem Skalar a, wenn es sich um die Matrizen α_ν bzw. mit dem Skalar b, wenn es sich um die Matrizen β_ν handelt, zu dividieren.

II

1. Wir werden nun versuchsweise allgemeiner setzen

$$(\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 m_0 c)(\beta_2 p_x + \beta_2 p_y + \beta_3 p_z + \beta_4 m_0 c) = 1\,\frac{u}{c} \,.\, \xi\,\frac{u}{c} \quad (6)$$

mit der Forderung der Vorschriften (für die quadratischen hermitischen Matrizen 4. Ordnung α_k und β_l)

$$\alpha_k \beta_l + \alpha_l \beta_k = 2\delta_{kl} \,.\, \xi \;\; (k, l = 1, 2, 3, 4) \qquad (7\,a)$$

Hier haben wir definiert

$$\alpha_k \beta_k = \xi \;\; (k, \; l = 1, 2, 3, 4) \qquad (7\,b)$$

und können gleich zeigen, dass es tatsächlich möglich ist, solche acht Matrizen zu finden; z. B.

$$\alpha_1 = \begin{Vmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{Vmatrix} \quad \alpha_2 = \begin{Vmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{Vmatrix} \quad \alpha_3 = \begin{Vmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{Vmatrix} \quad \alpha_4 = \begin{Vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{Vmatrix} \qquad (8\,a)$$

$$\beta_1 = \begin{Vmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{Vmatrix} \quad \beta_2 = \begin{Vmatrix} 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ -i & 0 & 0 & 0 \end{Vmatrix} \quad \beta_3 = \begin{Vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{Vmatrix} \quad \beta_4 = \begin{Vmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{Vmatrix} \qquad (8\,b)$$

mit

$$\xi = \begin{Vmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{Vmatrix}$$

Wir bemerken aber eben, dass die Matrix ξ nach der bekannten Regel[3] antihermitisch ist, denn sie entspricht dem antikommutativen Produkt $\alpha_k \beta_k$ (k, $1 = 1, 2, 3, 4$) hermitischer Matrizen α_k und β_k. Ebenso können wir bemerken, dass [also Folge der Definition (7 *b*)]

$$\xi\beta_k = -\beta_k\xi = \alpha_k \text{ und } \alpha_k\xi = -\xi\alpha_k = \xi \tag{9}$$

ist. Die Tatsache aber, dass die Matrix ξ eine antihermitische Matrix ist, steht keineswegs im Wege, denn wir werden weiter (unter 3) sehen, dass die Gleichungen, auf Grund der Matrizen α_r (kombiniert mit ξ) geschrieben, identisch sind mit den Gleichungen, die auf Grund der Matrizen β_r (kombiniert mit der Einheitsmatrix), also auf Grund aller hermitischer Matrizen geschrieben sind.

Es wird gezeigt, dass eine solche "assymetrische" Linearisation gemäss der Gleichung (6) zu den gleichen Resultaten führt wie die "symmetrische" Linearisation von *P. A. M. Dirac*, nur mit dem Unterschied, dass man sich durch Verwendung der Matrix ξ zugleich (d. h. in einer Ableitung) mit zwei Arten der Matrizen bedienen kann.

2. Das magnetische Moment des Elektrons (bzw. des Positrons) und die Diracsche Methode

Das magnetische Moment des Elektrons kann man entsprechend der hier vorgelegten Linearisation mittels der *Dirac*schen Methode so erhalten, dass man z. B. auf die Gleichung [wo $\mathrm{P}_r = \frac{\hbar}{i}\frac{\partial}{\partial x_r} - \frac{\epsilon}{c}\mathrm{A}_r$ ($r = 1, 2, 3$) und $\mathrm{P}_4 = -\frac{\hbar}{ic}\frac{\partial}{\partial t} - \frac{\epsilon}{c}\mathrm{V}$ die bekannten Operatoren bedeuten[4]]

$$(\beta_1\mathrm{P}_1 + \beta_2\mathrm{P}_2 + \beta_3\mathrm{P}_3 + \beta_4 m_0 c - \xi\mathrm{P}_4)\,\Psi = 0 \tag{10 a}$$

den Operator

$$(\alpha_1\mathrm{P}_1 + \alpha_2\mathrm{P}_2 + \alpha_3\mathrm{P}_3 + \alpha_4 m_0 c + \mathrm{P}_4) \tag{10 b}$$

(von der linken Seite) anwendet; man erhält so nach kurzer ffiechnung unter Beachtung von (7 *a*) und (7 *b*)

$$\begin{aligned}\{\xi(\mathrm{P}_1^2 + \mathrm{P}_2^2 + \mathrm{P}_3^2 + m_0^2c^2 - \mathrm{P}_4^2) + \alpha_1\beta_2(\mathrm{P}_1\mathrm{P}_2 - \mathrm{P}_2\mathrm{P}_1) \\ + \alpha_2\beta_3(\mathrm{P}_2\mathrm{P}_3 - \mathrm{P}_3\mathrm{P}_2) + \alpha_3\beta_1(\mathrm{P}_3\mathrm{P}_1 - \mathrm{P}_1\mathrm{P}_3) + \beta_1(\mathrm{P}_4\mathrm{P}_1 - \mathrm{P}_1\mathrm{P}_4) \\ + \beta_2(\mathrm{P}_4\mathrm{P}_2 - \mathrm{P}_2\mathrm{P}_4) + \beta_3(\mathrm{P}_4\mathrm{P}_3 - \mathrm{P}_3\mathrm{P}_4)\,\Psi = 0.\end{aligned} \tag{10 c}$$

Man kann sich leicht überzeugen, dass diese Gleichung vollkommen identisch ist mit der *Dirac*schen Gleichung 2. Ordnung, welche das das magnetische und das elektrische Moment des Elektrons ergibt. Man braucht nur diese Gleichung (10 *c*) von der rechten Seite der dort sich befindenden Matrizenprodukten mit $-\xi$ multiplizieren und man bekommt so [mit Rücksicht auf (9)]

$$\begin{aligned} &P_1^2 + P_2^2 + P_3^2 + m_0^2c^2 - P_4^2 + \alpha_1\alpha_2 (P_1P_2 - P_2P_1) \\ &+ \alpha_2\alpha_3 (P_2P_3 - P_3P_2) + \alpha_3\alpha_1 (P_3P_1 - P_1P_3) + \alpha_1 (P_4P_1 - P_1P_4) \\ &+ \alpha_2 (P_4P_2 - P_2P_4) + \alpha_3 (P_4P_3 - P_3P_4)\, \Psi = 0 \end{aligned} \tag{10 d}$$

Wir können aber in der Ableitung der Gleichung 2. Grades formal noch eine andere Kombination als bisher von den Matrizen α_ν und β_ν erhalten, wenn wir auf die Gleichung 1. Grades

$$(\alpha_1P_1 + \alpha_2P_2 + \alpha_3P_3 + \alpha_4m_0c - \xi P_4)\, \Psi = 0 \tag{11 a}$$

nochmals denselben Operator $\alpha_1P_1 + \alpha_2P_2 + \alpha_3P_3 + \alpha_4 m_0c - \xi P_4$ anwenden. Wir erhalten nach kurzer Rechnung

$$\begin{aligned} &\{P_1^2 + P_2^2 + P_3^2 + m_0^2c^2 - P_4^2 + \alpha_1\alpha_2 (P_1P_2 - P_2P_1) \\ &+ \alpha_2\alpha_3 (P_2P_3 - P_3P_2) + \alpha_3\alpha_1 (P_3P_1 - P_1P_3) + \beta_1 (P_4P_1 - P_1P_4) \\ &+ \beta_2 (P_4P_2 - P_2P_4) + \beta_3 (P_4P_3 - P_3P_4)\, \Psi = 0. \end{aligned} \tag{11 b}$$

Mit Rücksicht auf (9) können wir hier statt den Produkten $\alpha_k\alpha_l$ die Produkte $\beta_k\beta_l$ schreiben wodurch die Gleichung (11 *b*) identisch wird mit der *Dirac*schen Gleichung, wie man sie auf Grund der Matritzen β (kombiniert mit der Einheitsmatrix) erhalten kann.

3. Das Magnetische Moment des Elektrons und die Darwinsche Methode

Auch die bekannte *Darwin*sche Methode (5) zur Berechnung des magnetischen und des elektrischen Moments des Elektrons (bzw. des Positrons) kann man mittels der linearisierten Gleichungen (10 *a*) bzw. (11 *a*) anwenden. Um aber die Berechnungen in dieser Hinsicht zu vermeiden, kann man besser einen anderen Weg einschlagen, der sich als zweckmässig auch für andere Ableitungen zeigen wird. Wenn wir nämlich in der *Dirac*schen Gleichung

$$\begin{aligned} &(\beta_1p_x + \beta_2p_y + \beta_3p_z + \beta_4m_0c)\,(\beta_1p_x + \beta_2p_y + \beta_3p_z + \beta_4m_0c) \\ &= 1 \cdot \frac{u}{c} \cdot 1 \cdot \frac{u}{c} \end{aligned} \tag{12 a}$$

beiderseits den linken Faktor mit der Matrix ξ multiplizieren (die Multiplikation der Matrizen β_k mit ξ von der linken Seite durchgeführt gedacht), so erhalten wir inbezug auf (9), nach Gleichsetzen der linken und der rechten Faktoren auf beiden Seiten der so gewonnenen Gleichung und nach Durchführung notwendiger wohlbekannten Umformungen

$$(\alpha_1 P_1 + \alpha_2 P_2 + \alpha_3 P_3 + \alpha_4 m_0 c - \xi P_4)\, \Psi = 0 \qquad (12\,b)$$

$$(\beta_1 P_1 + \beta_2 P_2 + \beta_3 P_3 + \beta_4 mc - P_4)\, \Psi = 0 \qquad (12\,c)$$

Schreiben wir die so erhaltenen Gleichungen (12 *b*) und (12 *c*) gemäss den Matrizen (8 *a*) und (8 *b*) explizite auf, dann können wir gleich ersehen, dass einzelne Gleichungen dieser zwei Gruppen untereinander identisch sind, und zwar (der Reihe nach): die erste (zweite, dritte vierte) Gleichung aus (12 *b*) ist mit der dritten (vierten, ersten, zweiten) Gleichung aus (12 *c*) identisch. Die antihermitische Matrix ξ, kombiniert mit der hier vorgelegten hermitschen Matrizen α_r, bedeutet also nur eine andere Reihenfolge der *Dirac*schen Gleichungen, geschrieben auf Grund der Matrizen β_r (kombiniert mit der Einheitsmatrix). Da die zweite (β—) Gruppe der Gleichungen (12 *c*) zugleich vollkommen der *Dirac*schen Theorie entspricht so kann man selbstverständlich die *Darwin*sche Methode auf das Gleichungs-system (12 *b*) anwenden, weil sie auf das Gleichungssystem (12 *c*) anwendbar ist.

4. Das Magnetische Moment des Elektrons und die Methode des Wellenpaketes

Auf Grund des oben gesagten könnte es scheinen, dass es kaum vom Interesse sein könnte, weitere Ableitungen aus der *Dirac*schen Theorie auf Grund der hier vorgelegten Linearisation (d. h. mittels der Matrix ξ) zu explizieren. Aber Eines wäre sicher interessant und zwar die Ableitung der Kontinuitätsgleichung. Zu diesem Zweck denken wir die Gleichungen (12 *b*) der Einfachheit halber bei der Abwesenheit des elektromagnetischen Feldes aufgeschrieben und auch die ihnen konjugiert-komplex aufgeschriebenen Gleichungen. Dann denken wir die erste Gruppe von vier Gleichungen mit $\frac{i}{\hbar}$ und dann der Reihe nach mit $\dot{\Psi}_3$, $-\dot{\Psi}_4$, $-\dot{\Psi}_1$ und Ψ_2 multipliziert. Wir denken weiter die zweite Gruppe von vier (zu der ersten Gruppe konjugiert-komplex aufgeschriebenen Gleichungen) mit $-\frac{i}{\hbar}$ und der Reihe nach mit Ψ_3, $-\Psi_4$, $-\Psi_1$ und Ψ_2 multipliziert und addieren dann die alle nach der Multiplikation so gewonnenen Gleichungen. Der Grund dafür, warum wir nun eine andere Reihenfolge der Wellenfunktionen (Faktoren) nehmen, mit der wir die einzelnen Gleichungen multiplizieren,

als in der *Dirac*schen Theorie, ergibt sich, wenn wir die Sache etwas näher betrachten. In der *Dirac*schen Theorie entspricht nämlich die Reihenfolge der Wellenfunktionen (Multiplikatoren) der an die Einheitsmatrix sich anschliessenden Wellenfunktionen, und hier der Matrix ξ.

Man würde also auf diese Weise erhalten

$$\frac{\partial}{\partial x}\sum_{k=1}^{4}\dot{\Psi}_k\beta_1\Psi_k+\frac{\partial}{\partial y}\sum_{k=1}^{4}\dot{\Psi}_k\beta_2\Psi_k+\frac{\partial}{\partial z}\sum_{k=1}^{4}\dot{\Psi}_k\beta_3\Psi_k$$
$$+\frac{1}{c}\frac{\partial}{\partial t}\sum_{k=1}^{4}\dot{\Psi}_k\Psi_k=0. \qquad (12\,d)$$

Wir sind also von dem an die α-Gruppe der Matrizen sich anschliessenden Gleichungssystem (12 *b*) ausgegangen und sind zu der *Dirac*schen mittels der β-Gruppe der Matrizen ausgedrückten Kontinuitätsgleichung gelangt.

Der antihermitische Produkt ξ hermitischer Matrizen gemäss der Gleichung (7 *b*), wenn diese Matrizen die Bedingung (7 *a*) befriedigen, spielt also einigermassen die Rolle der "Kopplungsmatrix" zwischen den beiden *Dirac*schen Matrizensysteme α_ν und β_ν.

Auf die ganze andere Ableitung des magnetischen Moments des Elektrons, da sie vollkommen analog derjenigen ist, die schon aus der *Dirac*schen Theorie bekannt ist,[8] können wir selbstverständlich verzichten.

5. Andere Ableitungen

Mit Rücksicht darauf, was unter 3 gesagt ist, kann man auch die Ableitung des Spins, die Ungültigkeit des Theorems von *Ehrenfest*, die *Schrödinger*schen Oszillationen, die Feinstruktur der *Balmer*linien usw. ableiten.

Auf Grund alles dessen kann man also wohl den Schluss ziehen, dass die *Dirac*sche Linearisation zwar nicht notwendig zur Erreichung der brauchbaren Gleichungen für das Elektron und das Positron ist, mit Ausnahme, wenn man alle Matrizen hermitisch verlangt. In diesem Falle scheint sie auch notwendig zu sein.

6. Nochmals über die Antihermitizität der Matrix ξ

Man könnte eventuell zu allen diesen Ableitungen den Einwand machen, dass die Matrix ξ eine antihermitische Matrix ist und dass in der Quantenmechanik nur mit den hermitischen Matrizen zu operieren inst. Darauf muss man aber bemerken, dass man gerade auf diese Matrix ξ stösst, wenn man mit den *Dirac*schen Matrizen

$$\frac{\alpha_1+\beta_1}{\sqrt{2}},\ \frac{\alpha_2+\beta_2}{\sqrt{2}},\ \frac{\alpha_3+\beta_3}{\sqrt{2}},\ \frac{\alpha_4+\beta_4}{\sqrt{2}}$$

auf *Dirac*sche Art und Weise arbeitet. Will man nämlich nun die Methode des Wellenpaketes für die Berechnung des magnetischen Moments des Elektrons auf die *Dirac*schen Gleichungen

$$\left\{\frac{h}{i}\left(\frac{\alpha_1+\beta_1}{\sqrt{2}}\frac{\partial}{\partial x}+\frac{\alpha_2+\beta_2}{\sqrt{2}}\frac{\partial}{\partial y}+\frac{\alpha_3+\beta_3}{\sqrt{2}}\frac{\partial}{\partial z}\right)\right.$$
$$\left.+\frac{\alpha_4+\beta_4}{\sqrt{2}}m_0c+\frac{h}{ic}\frac{\partial}{\partial t}\right\}\Psi=0$$

anwenden, da braucht man mittels der Kombination der ersten und der dritten, dann der zweiten und der vierten Gleichung diejenigen Derivierten der Wellenfunktionen nach den Koordinaten eliminieren, die wir nicht als "primare" wählen wollen. Mathematisch viel einfacher und eleganter kann dies wohl durch die Multiplikation der letzten Gleichung von der linken Seite mit der Matrix

$$\xi_5=\begin{Vmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{Vmatrix}\frac{\alpha_1+\beta_1}{\sqrt{2}}$$

erfolgen; man erhält so

$$\frac{\hbar}{i}\left(\xi_1\frac{\partial}{\partial x}+\xi_2\frac{\partial}{\partial y}+\xi_3\frac{\partial}{\partial z}\right)+\xi_4 m_0c+\frac{h}{ic}\xi_5\frac{\partial}{\partial t}\Big\}\Psi=0;$$

$\xi_r\,(r=1,2,3,4)$ bedeuten die durch die Multiplikation erhaltenen Matrizen.

Erst aus dieser Gleichung können wir dann nach bekannter Methode[7] zwei "sekundäre" Wellenfunktionen auf Grund der zwei "primären" Wellenfunktionen mit beliebig gewählten Amplituden konstanten berechnen.

Dieselbe Transformation gilt auch für die Vorbereitung, wenn wir die *Darwin*sche Methode[8] der Berechnung des magnetischen Moments des Elektrons in etwas geänderter Form anwenden wollen.

Wir können aber gleich bemerken, dass die hiesige Matrix $\xi_3=-\xi$ ist, also eine antihermitische Matrix, die also in der weiteren Ableitung auftaucht, obzwar die Anfangsgleichungen die rein *Dirac*schen waren.

Dass man hie und da in der *Dirac*schen Theorie auf eine Antihermitizität stossen kann, ist schon bekannt.[9]

Zusammenfassung. Es wird gezeigt, wie man mittels zwei Gruppen von vier (*Dirac*schen) Matrizen, welche der Bedingung (7 *a*) genügen, operieren kann, um die brauchbaren Gleichungen für das Elektron und das Positron

zu gewinnen. Die Bedingung (7 *a*) ist eine Art der erweiterten *Dirac*schen Bedingung aufzufassen, weil sie in die *Dirac*sche Bedingung übergeht, falls wir $\alpha_k = \beta_k$ ($k = 1, 2, 3, 4$) voraussetzen; statt (7 *b*) soll man dann die Gleichung $\alpha_k^2 = 1$ schreiben.

LITERATUR

1. P. A. M. Dirac .. *Die Prinzipien d. Quantenmechanik*, 1930, 253.
2. L. de Broglie .. *Une nouvelle théorie de la lumière*, 1940, **1**, 65 ; *Particules à spin*, 1943, 12.
3. ———— .. *La théorie du noyau*, 1945, **11**, 29.
4. Cl. Schaefer .. *Theoretische Physik*, 1937, **III-2**, 463.
5. A. Haas .. *Ibid.*, 1930, **11**, 369 ; *Materiewellen u. Quantenmechanik*, 1930, 182 ; 1934, 187.
6. L. de Broglie .. *L' électron magnétique*, 1934, 170–77 ;
   Cl. Schaefer .. *Theoret. Physik.*, 1937, **III-2**, 468–75.
7. Vgl. 6/ ..
8. V. S. Vrkljan .. *Rad Jugosl. akademije*, 1949, 276, 187–93.
9. L. de Broglie .. *Une nouvelle théorie de la lumière*, 1940, **1**, 133; *L' électron magnétique*, 1934, 150–53.

RAMAN EFFECT IN MIXTURES OF ACETONE WITH ALCOHOLS

Hydrogen Bond Formation

By P. G. Puranik

(From the Physical Laboratories, Osmania University, Hyderabad)

Received February 26, 1953

(Communicated by Prof. S. Bhagavantam, F.A.SC.)

1. Introduction

Raman Effect and infra-red data have been successfully used in studying and explaining the intermolecular and intramolecular association caused by different processes. The formation of the hydrogen bond has received particular attention. Errera and Mollet (1936), Fox and Martin (1937), Williams, Hofstadter and Herman (1939) have studied the effect of polymerization in ethyl alcohol and phenol on the vibrations of the O—H linkage. Murthy and Sheshadri (1941) have recorded the Raman shifts in mixtures of esters and phenol, esters and alcohol, with a view to study the behaviour of carbonyl link. The bond formation in such mixtures is caused by the C = O group in the donor molecules and the O—H group in the acceptor molecules coming together. Consequently, the electron distribution gets readjusted and the carbonyl frequency in the donor gets reduced.

In the mixtures of acetone and phenol, the C = O frequency shifts from 1710 $cm.^{-1}$ to 1695 $cm.^{-1}$ Gordy (1938), from his study of infra-red absorption, has reported this shift of C = O absorption band. Koteswaram (1940) has studied the variation of the Raman Frequency due to the C = O linkage of acetone in aqueous solutions, and has reported a gradual decrease of the same with the reduction of acetone concentration.

Earlier workers had their attention generally confined to the C = O frequency, because hydrogen bond formation directly affects that linkage and weakens it, resulting in the decrease of the corresponding frequency. Koteswaram, however, has recorded a variation of the C—C frequency of acetone in aqueous solutions, and has mentioned that the admixture of acetone with methyl alcohol also indicates a decrease in the carbonyl frequency. But other investigators do not seem to have paid any attention to the variation in the C—C frequency, probably because the hydrogen bond formation effects this linkage only in an indirect manner. Even Koteswaram did not

proceed with higher alcohols and has not explained the implications of the increase in the C—C frequency.

The author, in a preliminary investigation, observed that both the C—C and C—H linkages in acetone are affected by the mixing of water and higher alcohols to a marked degree, in addition to the already well-known C = O linkage. This effect seems to be systematic, and not sporadic. It should, therefore, be regarded as consequential to the diminution of C = O frequency in mixtures. Thus, hydrogen bond formation can be studied with the help of a subsidiary effect, like that of the variation of C—C frequency, in addition to the direct effect on the carbonyl linkage. The C—C line has the added advantage of being twice as intense as the C = O line, particularly in acetone. It also occurs with visible excitation, in a region which is more convenient to study than the C = O frequency. Since the earlier work was done, more powerful techniques of getting intense Raman spectra have been developed, and the Raman lines can now be recorded within a few minutes. This enables one to study the finer features of the effect without taking recourse to prolonged exposures, and hence it is proposed by the author to examine some of these subsidiary effects, in their relation to hydrogen bond formation.

2. EXPERIMENTAL

Acetone, and all the alcohols used have been repeatedly distilled at their respective boiling points. Special care has been taken to render the alcohols free from water. Hilger Raman Source Unit, recently put on the market, has been used for illumination. There are four mercury vapour lamps (Mazda) in this Unit, arranged around a 22 cm. long Raman tube which can take in 7 c.c. of liquid. The lamps are arranged in series carrying a current of 10 amps. A Hilger E. 182 Littrow 2 metre spectrograph has been used to record the Raman spectra. A slit of 0·08 mm. width has been employed and comparison spectra obtained with the help of a Hartmann diaphragm. The plates are measured by direct comparison with a standard iron arc spectrum on a Hilger Comparator.

Moderately intense and sharp lines of 788 $cm.^{-1}$ (C—C) and 2925 $cm.^{-1}$ (C—H) for pure acetone are usually recorded in 30 minutes, and with the decrease of acetone content of the mixture, proportionately greater time is allowed for exposures, so that the intensity of the Raman lines in mixtures is almost the same as that of pure acetone. On account of such quick exposures, the broadening of the spectral lines due to prolonged photography and temperature variation has been eliminated.

3. Results

Water and five alcohols—methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl—have been chosen for studying the effect of their admixture with acetone. The results obtained by the author are given below. The C—C frequency and the C—H frequency of pure acetone, as obtained by the author, are 788 cm.$^{-1}$ and 2925 cm.$^{-1}$ respectively and these are in agreement with the average values of Kohlrausch.

Table I

Mixtures of Acetone with Water and Alcohols

% age by volume of acetone	C—C Frequency cm.$^{-1}$			C—H Frequency cm.$^{-1}$			C=O Frequency cm.$^{-1}$		
	80%	50%	20%	80%	50%	20%	80%	50%	20%
1. Water H·OH	795	799	801	2929	2935	2933	1704	1702	1696
2. Methyl alchhol CH_3·OH	794	795	799	2929	2934	2932	..	..	..
3. Ethyl alcohol C_2H_5·OH	788	788	788	2925	2925	2925	1710	1710	1710
4. *n*-Propyl alcohol C_3H_7·OH	788	792	794	2925	(2930)	(2930)	1710	1710	1706
5. *n*-Eutyl alcohol C_4H_9·OH	788	794	789	2925	(2926)	(2935)	1710	1710	1707

Note.—In the case of higher alcohols (4 and 5), there are Raman lines in the vicinity of C—H line of acetone. Such frequencies of acetone in mixtures, falling in the vicinity of the alcohol lines, are given in brackets. As the values may not be very reliable on account of possible overlapping, no detailed comments are made on these frequencies.

From the results detailed in Table I it is seen that

(i) The admixture of ethyl alcohol with acetone has no effect on any one of the acetone frequencies. This effect is being recorded for the first time in respect of C—C and C—H frequencies, but had been noticed in the case of C = O frequency, by earlier workers. Since ethyl alcohol is strongly polymerized by intermolecular association between two molecules of the alcohol, presumably there are no single molecules left for permitting any bond formation with the acetone molecules.

(ii) In the mixtures of methyl alcohol and water with acetone, the 788 cm.$^{-1}$ line and 2925 cm.$^{-1}$ line shift towards greater frequencies, with the lowering of the acetone concentration of the mixtures.

(iii) Higher alcohols like *n*-propyl alcohol and *n*-butyl alcohol, when mixed with acetone affect no shift in the C—C frequency of acetone, when the acetone content is very high. With the decrease in acetone concentration the C—C line shifts towards greater frequencies.

(iv) In the case of mixtures of *n*-amyl alcohol, the 788 line does not show any shift at higher concentrations of acetone. With the decrease in the acetone concentration the intensity of the acetone line becomes extremely weak.

(v) Spectrum of the scattered light in the case of mixtures exhibits a continuous background although the scattered beam in each of the pure substances separately does not give any continuous spectrum.

(vi) The phenomenon of concentration scattering, by which a mixture shows a disproportionate increase in the Rayleigh scattering but not in Raman scattering, is also shown very clearly in all the experiments with the mixtures. A quantitative investigation of this aspect is proposed to be made later.

4. DISCUSSION OF THE RESULTS

The author has observed, that in the mixtures studied, wherever there is a diminution of C = O frequency, there is always an increase in the C—C frequency. This means that the weakening of the carbonyl link due to the hydrogen bond formation, results in a strengthening of the C—C linkage, as is evidenced by the enhanced C—C frequency.

Exactly the same phenomenon is seen to occur when the carbonyl frequency is lowered similarly, though by a different process such as substitution of a benzene ring and such other groups in the ketone.

The Raman frequencies of C—C and C = O lines of a few substituted ketones studied by earlier workers are given in Table II.

A good number of substituted ketones other than those listed in Table II have been studied by earlier workers, but with only the C = O linkage in view, and not the C—C link. They will have to be re-examined from this point of view. The data given show that the diminution of the C = O frequency due to the substitution of certain radicals, is attended by an increase in the C—C frequency. The phenomenon now observed by the author in mixtures of acetone, with water and alcohols, with the exception of ethyl alcohol, is similar to such an effect. Only the shifts in the Raman frequencies of the C—C line are comparatively smaller. The larger shifts

TABLE II

Raman Frequencies of Acetone and Substituted Ketones

Name of the Ketone	Formula	Frequency	Frequency	Investigator
1. Acetone ..	$H_3C-\overset{\overset{O}{\parallel}}{C}-CH_3$	788	1706	Kohlrausch (1934)
2. Methyl benzyl ketone	$H_3C-\overset{\overset{O}{\parallel}}{C}-CH_2C_6H_5$	816	1697	Kohlrausch and Pongratz (1934)
3. 3. Octyn-2-one ..	$H_3C-\overset{\overset{O}{\parallel}}{C}-C\equiv C-C_4H_9$	809	1675	Murray and Cleaveland (1944)
4. 4. Nonyn-3-one ..	$H_5C_2-\overset{\overset{O}{\parallel}}{C}-C\equiv C-C_4H_9$	804	1675	do

in the substituted ketones can be attributed to a greater change in the magnitudes of valence forces. In the case of mixtures, the hydrogen bond formation being the cause, the effects are not so prominent.

The author expresses his sincere thanks to Prof. S. Bhagavantam for suggesting the problem and giving necessary guidance.

5. SUMMARY

The diminution of the C = O frequency in acetone due to hydrogen bond formation, when it is mixed with water or an alcohol, wherever it exists, is always accompanied by a corresponding increase of the C—C frequency. These phenomena appear to be related to each other because both of them are again noticed in substituted ketones, when the substitution is such that it lowers the frequency of the C = O line. It is suggested that these secondary changes may also be conveniently used for studying effects like hydrogen bond formation by Raman spectrum methods.

REFERENCES

1. Errera and Mollet .. *Nature*, 1936, **138**, 882.
2. Fox and Martin .. *J. Amer. Chem. Soc.*, 1937, **59**, 817.
3. Koteswaram .. *Ind. Jour. Phy.*, 1940, **14**, 333.
4. Kohlrausch and Pongratz .. *Monatsh*, 1934, **64**, 374.
5. Murthy and Sheshadri .. *Proc. Ind. Acad. Sci.*, 1941, **14**, 593.
6. ———— .. *Ibid.*, 1942, **15**, 154.
7. Murray and Cleaveland .. *Jour. Chem. Phy.*, 1944, **12**, 156.
8. Williams Gordy .. *J. Amer. Chem. Soc.*, 1938, **60**, 605.
9. Williams, Hofstadter and Herman .. *J. Amer. Chem. Phys.*, 1939, **6**, 110.

UNIVERSITY OF MICHIGAN LIBRARIES

A NEW VOLUMETRIC METHOD OF CERIUM DETERMINATION BY THIOCYANATE

By G. S. Deshmukh, D.Sc.

(Asst. Professor of Chemistry, Benares Hindu University)

AND

B. R. Sant, M.Sc.

Received February 26, 1952

[Communicated by Prof. S. S. Joshi, D Sc. (Lond.), F.R.I.C., F.A.Sc.]

Ceric sulphate is a valuable oxidant in quantitative analysis, because of its great stability[9, 10] and has almost supplanted permanganate and dichromate in certain analytical processes.[3, 4, 14]

Many quantitative analytical processes are based on the oxidation of thiourea and thiocyanates.[2, 12] In practically every case the sulphur atom of the anion is oxidized to sulphate, and in most cases the nitrogen escapes as hydrogen cyanide.[5]

Review of the literature showed that little data exist on the determination of cerium using thiocyanate. The addition of ammonium or potassium thiocyanate discharges the characteristic yellow colour of ceric sulphate, indicating its reduction to cerous condition. The possibility therefore, of using standard thiocyanate for the determination of cerium in a given ceric sulphate solution was studied.

Experimental

The ceric sulphate solution was prepared by digesting with concentrated sulphuric acid, a commercial sample containing about 40% ceric oxide as recommended by Willard and Young[11]; and standardised by titrating against ferrous ammonium sulphate of known strength, using *o*-phenanthroline ferrous complex or diphenylamine as the indicator.[7, 1] The thiocyanate solution was standardised by Volhard's method; and silver nitrate by the method of Mohr.

The end point in the titration of ceric sulphate against thiocyanate was found to depend on the way the thiocyanate was added. Whilst a rapid addition of thiocyanate entailed the possibility of overtitration, a slow dropwise addition took in a larger quantity of the reductant, leading to high results. Addition of the titre over a period ranging from 15 seconds to

30 minutes, offered no advantage, nor did the preheating of ceric sulphate solution. The following procedure was finally adopted:

A known excess (*a* ml.) of dilute thiocyanate solution was run in directly into (*b* ml.) of cold ceric sulphate solution with constant stirring till the yellow colour was discharged completely. This was followed by (*c* ml.) of silver nitrate (equivalent to *d* ml. of thiocyanate); the titration was finished by adding (*e* ml.) of thiocyanate, with ferric nitrate as the indicator.[8] The difference ($a + e - d$ ml.) was the thiocyanate required to reduce the ceric sulphate to cerous condition in terms of the equation

$$6\,Ce(SO_4)_2 + KCNS + 4\,H_2O \rightarrow 3\,Ce_2(SO_4)_3 + KHSO_4 + 3\,H_2SO_4 + HCN \quad (1)$$

Results of one representative series of experiments are returned in Table I.

TABLE I

Overall Acidity 2–3 *N* H_2SO_4

Expt. No.	Conc. of $Ce(SO_4)_2$	Normality of KCNS	Vol. of $Ce(SO_4)_2$ (*b* ml.)	Vol. of KCNS ($a+e-d$ ml.)	CeO_2 found gm.	CeO_2 Calcd. gm.	% Error
1	0·01840 N	0·01021	10	3	0·03163	0·03166	0·094
2	0·03572	0·01146	10	5·2	0·06153	0·06146	0·11
3	0·03793	0·01089	10	5·8	0·06523	0·06525	0·03
4	0·04592	0·01277	10	6·0	0·07889	0·07902	0·16
5	0·05500	0·01817	10	5·05	0·09473	0·09464	0·095
6	do.	do.	20	10·1	0·1894	0·18928	0·06
7	do.	do.	30	15·2	0·2852	0·28392	0·45
8	0·05792	0·01305	10	7·4	0·09968	0·09970	0·02
9	0·06219	0·01125	10	9·2	0·1069	0·1070	0·09
10	do.	do.	20	18·45	0·2142	0·2140	0·09
11	do.	do.	30	27·65	0·3211	0·3210	0·03
12	0·1111	0·01072	10	17·3	0·1914	0·1912	0·10
13	0·05500	0·01817	40	20·35	0·3819	0·37856	0·88
14	do.	do.	50	25·55	0·4793	0·4732	1·29
15	0·06219	0·01125	40	37·25	0·4325	0·4286	0·91
16	do.	do.	50	46·9	0·5448	0·5350	1·83

DISCUSSION

In the estimation of iron by thiocyanate, Peters and French[6] and Woods and Mellon[13] observed that $Ce^{\cdots}$, $(CN)'$ and SO_3'' ions did not interfere in the formation of ferric thiocyanate by more than 2%, when present in a concentration 250 times that of ferric ions.

In the present work, the detection of the end point and therefore, the accuracy of the result depends on the production of red ferric thiocyanate. It is suggested therefore, that the discrepancy between the observed and

the calculated results in Expts. 13–16, Table I, may be ascribed to the influence of the large concentration of $Ce^{\cdots}$ and/or SO_4'' ions.

It follows from equation (1), that with the completion of the reaction, the total number of sulphate ions increases from twelve to thirteen. A quantitative estimation of sulphate in the ceric sulphate solution, with and without the addition of thiocyanate, should therefore serve as a further test of the suggested reaction mechanism.

To an aliquot portion of ceric sulphate a requisite amount of thiocyanate is added and the sulphate precipitated as usual. A blank estimation, without the addition of thiocyanate, is simultaneously carried out. From the knowledge of the actual amount of ceric sulphate present, the increase in the weight of precipitated $BaSO_4$ due to the addition of thiocyanate is calculated. Typical results in Table II show that the agreement between the calculated and the observed values lies within the limits of experimental error.

TABLE II

Expt. No.	Amount of $Ce(SO_4)_2$ in 10 ml. (gm.)	Wt. of $BaSO_4$ without KCNS (gm.)	Wt. of $BaSO_4$ with KCNS		Difference
			Obsd. (gm.)	Calcd. (gm.)	
1	0·1525	0·2141	0·2354	0·2352	+0·0002
2	0·1992	0·2699	0·2965	0·2963	+0·0002
3	0·2138	0·2898	0·3182	0·3179	+0·0003

Since the determination of cerium is based on the oxidation-reduction reaction, the presence of other trivalent rare earths—its almost invariable contaminants, does not affect the accuracy of the results.

A comparative study of the methods of estimation of thiocyanate by $KMnO_4$[12] and ceric sulphate shows that under identical experimental conditions one molecule of KCNS is equivalent to 6/5 and 6 molecules of permanganate and $Ce(SO_4)_2$ respectively; the utilisability of the latter in the determination of small quantities of thiocyanates is suggested. Experimental data given in Table I have been used in assessing the accuracy of the titration for the determination of thiocyanate, the ceric sulphate being assumed to be pure. It has been found that the method is quite accurate for the determination of thiocyanate. The above method indicates also an interesting possibility of silver estimation by ceric sulphate; this has already been confirmed by preliminary results of our investigation.

Grateful thanks of the authors are due to Professor S. S. Joshi for facilities, advice and kind interest in the work, and to the National Institute of Sciences of India for an award of a Fellowship to one of us (G. S. D.).

Summary

A new volumetric method for cerium determination, based on the reduction of ceric sulphate by potassium or ammonium thiocyanate added in excess and the determination of the excess by back-titration as in Volhard's method is developed. One molecule of KCNS reacts with six molecules of $Ce(SO_4)_2$; the sulphur atom of the thiocyanate is oxidized to sulphate. $Ce^{\cdots}$ and SO_4'' ions in moderate quantities and the usual rare earth impurities in ceric sulphate do not affect the accuracy of the method. The possibility of using ceric sulphate in the determination of small quantities of thiocyanate and in argentometric titration is suggested.

References

1. Berry .. *Analyst*, 1929, **54**, 461.
2. Cuthill and Atkins .. *J. Soc. Chem. Ind.*, 1937, **56**, 5 T.
3. Furman .. *J. Amer. Chem. Soc.*, 1928, **50**, 755.
4. ——— and Wallace .. *Ibid.*, 1929, **51**, 1449.
5. Hall .. *Ind. Eng. Chem. Anal. Ed.*, 1938, **10**, 395.
6. Peters and French .. *Ibid.*, 1941, **13**, 604.
7. Smith and Getz .. *Ibid.*, 1938, **10**, 304.
8. Vogel .. *A Text-Baok of Quantitative Inorganic Analysis*, Longmans, Green & Co., 1945, 319.
9. Willard and Young .. *J. Amer. Chem. Soc.*, 1929, **51**, 149.
10. ——————— .. *Ibid.*, 1933, **55**, 3260.
11. ——————— .. *Ibid.*, 1928, **50**, 1322.
12. Williams .. *Cyanogen Compounds*, Edward Arnold & Co., London, 1948, **388**, 392.
13. Woods and Mellon .. *Ind. Eng. Chem. Anal. Ed.*, 1941, **13**, 551.
14. Young .. *J. Chem. Edu.*, 1934, **11**, 466.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

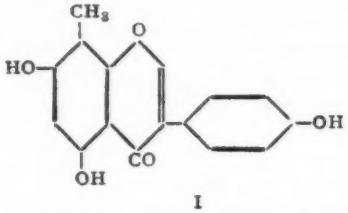
Part XXIII. A New Synthesis of 8-Methyl Genistein

By T. R. Seshadri, F.A.Sc. and S. Varadarajan

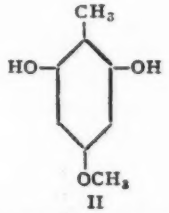
(From the Department of Chemistry, University of Delhi, Delhi)

Received November 5, 1952

Okano and Beppu[1] isolated four crystalline substances from soya beans and considered them to be isoflavones. To one of these, they assigned the constitution of 8-methyl genistein (I) on the basis of degradation studies. Later Shriner and Hull[2] reported a synthesis of a compound of this structure starting from C-methyl phloroglucinol α-methyl ether (II) and *p*-methoxy phenyl acetonitrile. They found that the melting points of the synthetic isoflavone and its triacetate were in agreement with those reported for the natural substance and its acetate.



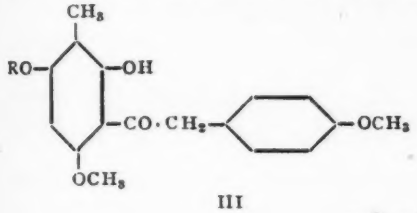
I



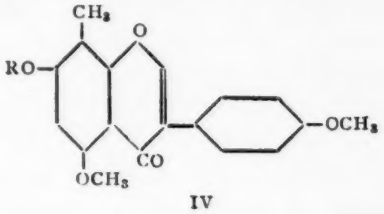
II

In an earlier publication[3] was described a synthesis of 8-methyl genistein, in which nuclear methylation of 2:4:6-trihydroxy-4′-methoxy phenyl benzyl ketone was used as a step. However the products of this synthesis were quite different from the natural compound and its derivatives and from the synthetic substance reported by Shriner and Hull.[2] In view of these discrepancies, it was thought necessary to re-examine the synthesis of 8-methyl genistein of Shriner and Hull.[2] For this purpose, the α-monomethyl ether of C-methyl phloroglucinol (II) has been made by the action of dry hydrogen chloride on an absolute methyl alcoholic solution of C-methyl phloroglucinol according to the method of Weidel[4] as modified by Curd and Robertson.[5] It is condensed with *p*-methoxy phenyl acetonitrile[3] under the conditions of Hoesch reaction. The product could be separated into two fractions: (i) soluble in aqueous sodium carbonate and (ii) soluble in aqueous sodium hydroxide. Fraction (i) gives a crystalline solid melting at 87–88°, with a negative ferric reaction and is identical with *p*-methoxy phenyl acetic acid.

Fraction (ii) yields 2: 4-dihydroxy-3-methyl-6: 4′-dimethoxy phenyl benzyl ketone (III *a*). It gives a positive reaction with ferric chloride and is found to melt at 162–64°. Shriner and Hull[2] reported that their compound of this structure melted at 125–27°. These authors did not note *p*-methoxy phenyl acetic acid as one of the products of the reaction and it is possible that their ketone sample had a lower melting point due to admixture with the acid.



III

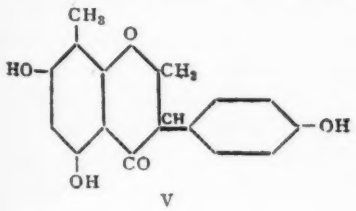


IV

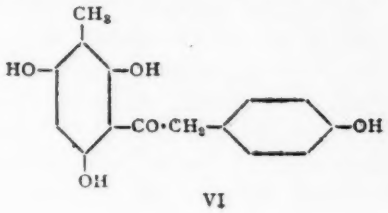
a, R = H
b, R = CH_3

On methylation with methyl iodide and potassium carbonate in acetone solution, (III *a*) yields 2-hydroxy-3-methyl-4 : 6 : 4′-trimethoxy phenyl benzyl ketone (III *b*), in every way identical with the product described in our earlier paper.[3] This establishes the authenticity of the ketone (III *b*) and it also proves that the synthesis of 8-methyl genistein (I) described in Part XXII[3] is quite unambiguous and there is really no discrepancy between that synthesis and the method of Shriner and Hull.[2]

To settle the question more definitely, 2: 4-dihydroxy-3-methyl-6: 4′-dimethoxy phenyl benzyl ketone (III *a*) has now been condensed with ethyl formate in presence of sodium.[6] The product is soluble in aqueous sodium hydroxide and does not give any colour with ferric chloride. It should therefore be 8-methyl-5: 4′-dimethoxy-7-hydroxy isoflavone (IV *a*). It melts at 287–90°. Shriner and Hull[2] however recorded that their substance melted at 268–72°. No compound having this melting point could be isolated in the present work. On methylation, the above dimethyl ether (IV *a*) yields 8-methyl-5: 7: 4′-trimethoxy isoflavone (IV *b*) identical with the product described in Part XXII.[3] Thus the two methods give rise to the same compounds and there is total agreement. There is therefore no



V



VI

doubt regarding the authenticity of 8-methyl genistein (I) obtained synthetically.[3] The earlier results of Shriner and Hull[2] are therefore difficult to explain.

These experiments also conclusively prove that the natural isoflavone isolated by Okano and Beppu[1] cannot have the constitution 8-methyl genistein (I). The degradation reactions carried out by Okano and Beppu[1] with the natural compound can be equally well explained if it was an isoflavanone, *i.e.*, if it had the structure of 8-methyl-5:7:4′-trihydroxy isoflavanone (V) since a compound of this structure can also give rise to 2:4:6:4′-tetrahydroxy-3-methyl phenyl benzyl ketone (VI). Complex isoflavanone derivatives, *e.g.*, rotenone and its allies, have long been known to occur in nature.

The existence of simpler isoflavanones has been shown by the recent study of padmakastein, isolated by Narasimhachari and Seshadri.[7] A synthesis of the tetrahydroxy ketone (VI) should throw some light on the structure of the natural compound from soya beans. This has now been attempted by the demethylation of 2:4:6-trihydroxy-3-methyl-4′-methoxy phenyl benzyl ketone[3] with aluminium chloride in benzene solution. Due to the very poor solubility of this ketone in benzene, demethylation does not take place. However, the required tetrahydroxy compound (VI) could be obtained by employing the easily soluble methyl ether (III *b*) for this demethylation. The product is readily soluble in sodium carbonate and melts at 235–37°. Okano and Beppu[1] stated that their tetrahydroxy ketone melted at 190°. It is possible therefore that the natural compound isolated by them is not an isoflavone or isoflavanone but has a different structure.

EXPERIMENTAL

2:4-Dihydroxy-3-methyl-6:4′-dimethoxy phenyl benzyl ketone (III a)

To a solution of C-methyl phloroglucinol α-monomethyl ether (II)[5] (3·8 g.) and *p*-methoxy phenyl acetonitrile[3] (5·5 g.) in dry ether (150 c.c.) was added powdered fused zinc chloride (1·5 g.). The mixture was cooled in an ice-bath and dry hydrogen chloride was passed in for 5 hours. It was then left in the ice-chest for 15 hours. Dry ether (100 c.c.) was then added to precipitate the ketimine hydrochloride completely. An oil mixed with some crystals separated. The ether portion was decanted off and the ketimine hydrochloride washed with dry ether twice. Water (150 c.c.) was added and the mixture heated under reflux in a boiling water-bath for 1·5 hours. On cooling, a red oil separated. It did not solidify on keeping at 0° for a number of hours. The mixture was extracted with ether and the ether solution washed first with aqueous sodium carbonate thrice. The carbonate solution was acidified, extracted with ether and ether distilled.

The residue crystallised from 75% alcohol (charcoal) and melted at 87–88°. It dissolved in aqueous sodium bicarbonate and did not give any colour with ferric chloride. A mixture of the substance with an authentic sample of *p*-methoxy phenyl acetic acid also melted at 87–88°.

The original ether solution remaining after extraction with sodium carbonate was then extracted with aqueous sodium hydroxide (10%) thrice. The combined deep red alkaline extract was cooled to 0° and acidified with hydrochloric acid. The reddish sticky solid that was precipitated was filtered and washed with water. On macerating with cold alcohol, the coloured impurities dissolved. The colourless solid was filtered, washed with a small quantity of cold alcohol and crystallised from dilute alcohol when 2: 4-dihydroxy-3-methyl-6: 4′-dimethoxy phenyl benzyl ketone separated as fine feathery colourless needles and long rectangular rods melting at 162–64°. Shriner and Hull[2] gave the melting point as 125–27°. It was easily soluble in alcohol and it gave a pinkish brown ferric reaction in alcoholic solution. A solution of the substance in aqueous sodium hydroxide was colourless (Found: C, 67·9; H, 6·2; $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%).

2-Hydroxy-3-methyl-4: 6: 4′-trimethoxy phenyl benzyl ketone (III b)

A solution of the above dihydroxy ketone (III *a*) (0·2 *g.*) in acetone (75 c.c.) was treated with methyl iodide (1·0 c.c.) and potassium carbonate (2 g.) and the mixture refluxed for two hours. The solution was filtered and the solid residue washed with acetone. The oil left on distilling off the solvent was treated with water (100 c.c.) and the solid so obtained was filtered after two hours. It crystallised from alcohol as colourless rectangular rods melting at 114–15° and a mixture of the substance with 2-hydroxy-3-methyl-4: 6: 4′-trimethoxy phenyl benzyl ketone[3] had the same melting point. Yield 0·2 g.

5: 4′-Dimethoxy-7-hydroxy-8-methyl isoflavone (IV a)

A suspension of 2: 4-dihydroxy-3-methyl-6: 4′-dimethoxy phenyl benzyl ketone (0·6 g.) in freshly distilled ethyl formate (15 c.c.), cooled to 0° was gradually added with stirring to powdered sodium (0·5 g.). The mixture was stirred for one hour and left in the ice-chest for 48 hours. Pieces of ice and hydrochloric acid (15 c.c.) were then added and the mixture stirred well and left overnight. Unreacted ethyl formate was evaporated under reduced pressure and the dark solid was filtered after cooling. It was macerated with cold alcohol and filtered and the residue crystallised from boiling alcohol. 5 : 4′-Dimethoxy-7-hydroxy-8-methyl isoflavone (IV *a*) was obtained in the form of colourless rhombic prisms melting at 287–90°

(decomp.). Shriner and Hull[2] have reported the melting point of this substance to be 268–72°. Yield 0·15 g. It was sparingly soluble in alcohol and easily soluble in acetone. It did not give any colour with alcoholic ferric chloride and was soluble in aqueous sodium hydroxide (Found: C, 68·8; H, 5·0; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

Methylation

The above compound (0·1 g.) in acetone (100 c.c.) was heated under reflux with methyl iodide (0·3 c.c.) and potassium carbonate (1 g.) for 3 hours. The potassium salts were filtered off and washed with acetone. The solvent was distilled off from the combined filtrate and water (60 c.c.) added to the residue. The precipitate was collected and crystallised from alcohol. It separated as colourless thick prisms melting at 181–83° and the mixed melting point with a sample of 8-methyl-5:7:4′-trimethoxy isoflavone[3] was not depressed.

2:4:6:4′-*Tetrahydroxy-3-methyl phenyl benzyl ketone* (*VI*)

To a solution of 2-hydroxy-3-methyl-4:6:4′-trimethoxy phenyl benzyl ketone (III *b*)[3] (0·4 g.) in dry benzene (30 c.c.), well powdered anhydrous aluminium chloride (1·6 g.) was added and the mixture refluxed on a water-bath for 2 hours. Benzene was then distilled off and the aluminium chloride complex decomposed by the addition of ice and hydrochloric acid. The tetrahydroxy ketone that separated was filtered and purified by dissolving in aqueous sodium carbonate (10%). Yield 0·2 g. When crystallised from dilute alcohol twice, it was obtained as pale yellow rectangular rods and prisms melting at 235–37°. It gave a deep pink colour with alcoholic ferric chloride and a solution of the substance in aqueous sodium carbonate was pale yellow (Found: C, 66·1; H, 5·4; $C_{15}H_{14}O_5$ requires C, 65·7; H, 5·1%).

SUMMARY

In view of the discrepancies between the products of the synthesis of 8-methyl genistein described in Part XXII and those of Shriner and Hull, the method of these authors has been re-examined. 2:4-Dihydroxy-3-methyl-6:4′-dimethoxy phenyl benzyl ketone and 5:4′-dimethoxy-7-hydroxy-8-methyl isoflavone prepared now are found to have melting points much higher than those reported by Shriner and Hull. However, on methylation, they yield their respective monomethyl ethers which are identical with those described in Part XXII. There is thus complete agreement between the two syntheses.

The natural compound of Okano and Beppu cannot be 8-methyl genistein. However the degradation reac ions could be explained on the

basis of an isoflavanone structure. In order to make sure of the primary degradation product, *viz.*, 2:4:6:4'-tetrahydroxy-3-methyl phenyl benzyl ketone, it has now been synthetically obtained from its trimethyl ether by demethylation with aluminium chloride. But the synthetic product is found to be different from the tetrahydroxy ketone of Okano and Beppu and therefore the natural compound may not be a simple isoflavone or isoflavanone but may have a different structure.

References

1. Okano and Beppu .. *J. Agri. Chem. Soc. Japan*, 1939, **15**, 645.
2. Shriner and Hull .. *J. Org. Chem.*, 1945, 228.
3. Seshadri and Varadarajan .. *Proc. Ind. Acad. Sci.*, 1953, **37A**, 145.
4. Weidel .. *Monatsh*, 1898, **19**, 223.
5. Curd and Robertson .. *J.C.S.*, 1933, 437.
6. Venkataraman *et al.* .. *Ibid.*, 1934, 513 *and* 1770.
7. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **35 A**, 202.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXIV. A Synthesis of Isogenistein

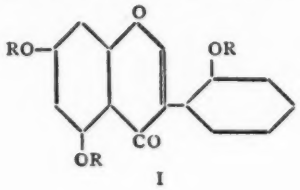
By T. R. Seshadri, F.A.Sc. and S. Varadarajan

(From the Department of Chemistry, University of Delhi, Delhi)

Received November 13, 1952

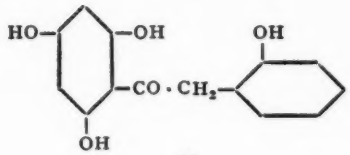
Among the benzopyrone derivatives containing the C_{15} skeleton, compounds having a hydroxyl group in the 2′-position are rare. Two such are the flavonols datiscetin[1] and morin.[2] As belonging to this type among isoflavones have been reported two substances isogenistein and 8-methyl isogenistein, isolated from soya beans.[3]

Isogenistein occurs as its glucoside isogenistin from which it is obtained by acid hydrolysis. Analytical values and molecular weight determination indicated that it had the formula $C_{15}H_{10}O_5$. It yielded a triacetate and a dimethyl ether. Degradation of isogenistein (I *a*) with alkali gave formic acid and 2:4:6:2′-tetrahydroxy phenyl benzyl ketone (II) which could be further degraded into phloroglucinol and *o*-hydroxy phenyl acetic acid (III). Based on these reactions, Okano and Beppu[3] assigned it the constitution of 5:7:2′-trihydroxy isoflavone (I *a*).

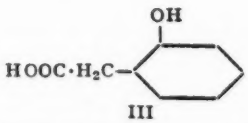


I

a, R = H
b, R = CH_3



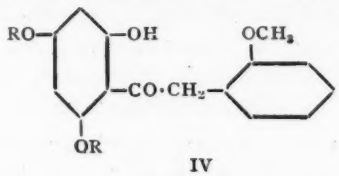
II



III

A synthesis of isogenistein has now been undertaken and it follows the same lines as the synthesis of genistein by Narasimhachari and Seshadri.[4] The starting point for the present work is 2:4:6-trihydroxy-2′-methoxy phenyl benzyl ketone (IV *a*) which has been made by the Hoesch condensation of phloroglucinol with *o*-methoxy phenyl acetonitrile. This nitrile was originally made by Pschorr, Wolfes and Buckow[5] from the difficultly accessible *o*-methoxy benzyl chloride by treatment with potassium cyanide. More

recently it has been prepared by the azlactone method[6] from *o*-methoxy benzaldehyde by Bergel, Haworth, Morrison and Rinderknecht[7] and this has been adopted for the present work. The above authors did not isolate and characterise the intermediate *o*-methoxy phenyl pyruvic acid and its oxime. It is found that the pyruvic acid is a liquid. The oxime is obtained as a solid but attempts to crystallise it yield a product melting at 69–70°. The melting point and the analytical values prove it to be identical with *o*-methoxy phenyl acetonitrile, showing that the oxime is very unstable and loses water and carbon dioxide even during crystallisation.



IV

a, R=H
b, R=CH_3

On methylation with two moles of dimethyl sulphate in acetone medium, the trihydroxy ketone (IV *a*) yields 2-hydroxy-4 : 6: 2′-trimethoxy phenyl benzyl ketone (IV *b*). It gives a blue colour with concentrated nitric acid and exhibits a wine red ferric reaction. These properties are in agreement with its structure. Condensation of the ketone (IV *b*) with ethyl formate and sodium[8] gives rise to a good yield of 5: 7: 2′-trimethoxy isoflavone (I *b*). It crystallises with one molecule of water which is very tenaciously held and is not lost even on drying at 120° *in vacuo* for 2 hours.* It melts at 180–81°. Okano and Beppu[3] did not prepare the trimethyl ether of the natural compound and no comparison is therefore possible.

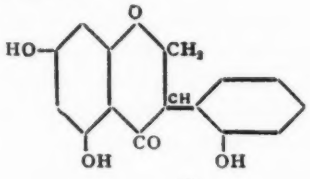
Demethylation of the trimethyl ether (I *b*) offered considerable difficulty. On boiling with acetic anhydride and hydriodic acid, it yields a resinous product from which a very small amount of crystalline compound melting at 222–23° could be isolated. This is soluble in aqueous sodium carbonate and gives an initial pink colour with alcoholic ferric chloride which changes to pale brown. These properties indicate that it is 5: 7: 2′-trihydroxy isoflavone (I *a*). Repetition of the experiment using larger amounts of acetic anhydride and hydriodic acid does not bring about any change in the results. Some complex changes besides demethylation seem to be taking place to a certain extent.

The alternative method of demethylation using aluminium chloride in benzene solution[9] has been next attempted. Here also due to the very low

* It has subsequently been found that the substance is not a hydrate of 5: 7: 2′-trimethoxy isoflavone, but is actually 2-hydroxy-5: 7: 2′-trimethoxy-isoflavanone.

solubility of the trimethyl ether (I *b*) in benzene, at first there was not much success. However, by employing a very large quantity of the hot solvent and by adding aluminium chloride to a constantly stirred mixture of the compound and the solvent and then refluxing for 2 hours, the demethylation has been successfully carried out. The product has been purified by dissolution in aqueous sodium carbonate. It also melts at 222–23° and is in every way identical with the product obtained by demethylation of the trimethyl ether (I *b*) with hydriodic acid. The identity of the products obtained by the two methods therefore definitely establishes that they are both 5 : 7 : 2′-trihydroxy isoflavone (I *a*). Okano and Beppu[3] however recorded the melting point of the natural compound as 302° and the ferric reaction to be violet. These differences definitely establish that the natural substance of Okano and Beppu cannot be 5 : 7 : 2′-trihydroxy isoflavone.

It is possible that the naturally occurring substance is an isoflavanone (V) which would account for the formation of 2 : 4 : 6 : 2′-tetrahydroxy phenyl benzyl ketone (II) by alkali degradation (see Part XXIII[10]). To test this possibility, the tetrahydroxy ketone (II) has now been synthetically obtained by the demethylation of 2-hydroxy-4 : 6 : 2′-trimethoxy phenyl benzyl ketone (IV *b*) with aluminium chloride in benzene solution. It is found to melt at 217–20° whereas the tetrahydroxy ketone obtained by Okano and Beppu[3] has been reported to melt at 182–83°.



V

In view of these differences, it can be said that the natural compound is not a simple isoflavone or isoflavanone but it is of a different nature.

EXPERIMENTAL

o-*Methoxy phenyl acetonitrile*

The starting material for this preparation, *viz.*, *o*-methoxy benzaldehyde was made according to the method of Dickinson and Marshall,[11] who reported its boiling point to be 242–45°. It is now found to distil at 236–37° as described by Shoesmith and Connor.[12] 2-Phenyl-4-(*o*-methoxy benzal)-oxazolone was prepared earlier from this aldehyde by Mauthner[13] who gave the melting point of the oxazolone as 165–66°. More recently Bergel *et al.*[7] have reported its melting point to be 156–57°. It has now been prepared by

heating together *o*-methoxy benzaldehyde (30 g.), hippuric acid (45 g.), fused sodium acetate (15 g.) and acetic anhydride (75 c.c.). It crystallised from alcohol as bright yellow prisms melting at 165–66°. Yield 42 g. It was hydrolysed by boiling with sodium hydroxide solution (22 g. in 130 c.c. of water) for an hour and *o*-methoxy phenyl pyruvic acid was separated from benzoic acid through its bisulphite compound. Yield 14 g. The pyruvic acid was a heavy yellow oil and it was converted into its oxime by heating with aqueous sodium hydroxide (150 c.c. of 8%). Attempts to crystallise the oxime from dilute alcohol yielded *o*-methoxy phenyl acetonitrile as thin colourless rectangular prisms melting at 69–70° alone or when mixed with an authentic sample of the nitrile, prepared according to the method of Bergel *et al.*,[7] by heating the oxime with acetic anhydride (Found: C, 73·1; H, 6·3; C_9H_9ON requires C, 73·5; H, 6·1%).

2:4:6-*Trihydroxy*-2′-*methoxy phenyl benzyl ketone* (*IV a*)

To a solution of dry phloroglucinol (12 g.) and *o*-methoxy phenyl acetonitrile (12 g.) in dry ether (150 c.c.) was added powdered, fused zinc chloride (2 g.). The mixture was cooled to 0° and a stream of dry hydrogen chloride passed in for 5 hours. On leaving overnight at 0°, the ketimine hydrochloride separated as a dark red oil. The upper layer of ether was decanted off. The ketimine hydrochloride was washed twice with dry ether and heated with water (150 c.c.) on a boiling water-bath for 4 hours. On cooling, a pale yellow solid separated. It was filtered and crystallised from dilute alcohol. 2:4:6-Trihydroxy-2′-methoxy phenyl benzyl ketone was obtained as pale yellow prisms melting at 168–70°. Yield 11·5 g. It gave a deep pink ferric reaction in alcoholic solution and dissolved in dilute sodium carbonate to give a pale yellow solution (Found: C, 61·9; H, 5·6; loss on drying at 120° for 2 hours *in vacuo*, 5·9; $C_{15}H_{14}O_5$, H_2O requires C, 61·7; H, 5·5; loss of H_2O, 6·2%).

2-*Hydroxy*-4:6:2′-*trimethoxy phenyl benzyl ketone* (*IV b*)

The above trihydroxy ketone (2 g.) in dry acetone (150 c.c.) was treated with dimethyl sulphate (1·4 c.c., 2 moles) and potassium carbonate (7 g.) and the mixture refluxed for four hours. The potassium salts were filtered and washed with warm acetone. The solvent was distilled off from the filtrate and the residue crystallised from alcohol twice. 2-Hydroxy-4:6:2′-trimethoxy phenyl benzyl ketone separated as sheaves of thin colourless plates melting at 116–18°. Yield 1·45 g. It gave a wine red colour with ferric chloride in alcoholic solution. It was insoluble in aqueous sodium hydroxide (10%). It gave a blue colour with concentrated nitric acid (Found: C, 67·8; H, 6·3; $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%).

5:7:2′-*Trimethoxy isoflavone* (*I b*)*

A suspension of the above ketone (1·5 g.) in ethyl formate (25 c.c.) was treated with powdered sodium (1 g.) at 0° and the mixture left in the refrigerator for 48 hours. Ice and hydrochloric acid (10 c.c.) were then added and the excess of ethyl formate distilled under reduced pressure. The precipitate was collected and crystallised twice from alcohol, when 5:7:2′-trimethoxy isoflavone came out as colourless rectangular rods melting at 180–81°. Yield 1·1 g. It was sparingly soluble in alcohol, benzene and ethyl acetate. It did not give any colour with alcoholic ferric chloride. No blue or green colour was produced when concentrated nitric acid was added to the substance (Found in a sample dried at 110° *in vacuo*: C, 65·9; H, 5·9; $C_{18}H_{16}O_5$, H_2O requires C, 65·5; H, 5·5%).

5:7:2′-*Trihydroxy isoflavone* (*Isogenistein*) (*I a*)

(i) To a suspension of well powdered 5:7:2′-trimethoxy isoflavone (1 g.) in hot benzene (200 c.c.), powdered anhydrous aluminium chloride (4·3 g.) was added in small lots with constant shaking. The complex began to separate as a greenish yellow solid. The mixture was refluxed on a water-bath for 4 hours. Benzene was then distilled off and the residue cooled and treated with ice and hydrochloric acid (10 c.c.). On leaving overnight, a colourless solid separated. It was filtered and treated with aqueous sodium carbonate. Undissolved impurities were filtered off and the filtrate on acidification yielded 5:7:2′-trihydroxy isoflavone. When crystallised thrice from dilute alcohol, it was obtained as short pale yellow needles sintering at 183° and melting at 222–23°. Yield 0·4 g. It gave a deep pink colour with alcoholic ferric chloride which changed to pale brown on the addition of excess of the reagent (Found: C, 64·8; H, 4·2; loss on drying at 120° in vacuum for 6 hours, 3·7; $C_{15}H_{10}O_5$, $\frac{1}{2}H_2O$ requires C, 64·5; H, 3·9; loss of H_2O, 3·2%).

(ii) To a solution of 5:7:2′-trimethoxy isoflavone (1 g.) in acetic anhydride (25 c.c.), hydriodic acid (37 c.c., d. 1·7) was added cautiously and the mixture heated at 140–50° in an oil-bath for 2 hours. It was then cooled and treated with an aqueous solution of sodium bisulphite (120 c.c.). After 48 hours, the dark brown solid was filtered and purified by dissolution in aqueous sodium carbonate (10%). The trihydroxy isoflavone crystallised from dilute alcohol (charcoal) as short pale yellow needles sintering at 183° and melting at 222–23° alone or when mixed with a sample obtained in (i) above. Yield 70 mg.

* Please see footnote in an earlier page.

2:4:6:2′-*Tetrahydroxy phenyl benzyl ketone* (*II*)

To a solution of 2-hydroxy-4:6:2′-trimethoxy phenyl benzyl ketone (1 g.) in dry benzene (25 c.c.) was added anhydrous aluminium chloride (3 g.). The mixture was refluxed for 2 hours. The residue left on distilling off benzene was treated with ice and hydrochloric acid and the tetrahydroxy ketone so obtained was purified by dissolution in aqueous sodium carbonate. It was crystallised twice from alcohol and then twice from a mixture of ethyl acetate and benzene. It separated as short colourless needles melting at 217–20° (decomp.). Yield 0·3 g. It was easily soluble in alcohol and ethyl acetate and sparingly soluble in benzene and petroleum ether (Found in a sample dried at 120° *in vacuo* for 6 hours: C, 65·0; H, 4·9; $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·6%).

Summary

One of the substances occurring in soya beans has been considered by Okano and Beppu to be 5:7:2′-trihydroxy isoflavone (isogenistein), based on degradation studies. A compound of this structure has now been made starting from 2:4:6-trihydroxy-2′-methoxy phenyl benzyl ketone. Partial methylation, treatment with ethyl formate and sodium followed by demethylation yield the required isoflavone. Aluminium chloride in benzene solution is found to be a much better reagent than hydriodic acid for the above demethylation. The products of the present synthesis are found to be different from the natural compound and its derivatives. Therefore the natural compound cannot be an isoflavone of this constitution. The main degradation product, considered to be 2:4:6:2′-tetrahydroxy phenyl benzyl ketone by Okano and Beppu differs considerably from a synthetic product of this constitution. Hence the natural compound cannot be a simple isoflavone or isoflavanone and should have a different structure.

References

1. Kalff and Robinson .. *J.C.S.*, 1925, 1968.
2. Robinson and Venkataraman .. *Ibid.*, 1929, 61.
3. Okano and Beppu .. *J. Agri. Chem. Soc. Japan*, 1939, **15**, 645.
4. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1950, **32A**, 256.
5. Pschorr, Wolfes and Buckow .. *Ber.*, 1900, **33**, 166.
6. Baker and Robinson .. *J.C.S.*, 1929, 357.
7. Bergel, Haworth, Morrison and Rinderknecht .. *Ibid.*, 1944, 263.
8. Venkataraman *et al.* .. *Ibid.*, 1934, 513 and 1770.
9. Seshadri *et al.* .. *Proc. Ind. Acad. Sci.*, 1947, **24A**, 213; 1947, **25A**, 432; 1949, **29A**, 72; 1952, **35A**, 34, 82 and 202.
10. Seshadri and Varadarajan .. *Ibid.*, 1953, **37A**, 508.
11. Dickinson and Marshall .. *J.C.S.*, 1929, 1496.
12. Shoesmith and Connor .. *Ibid.*, 1929, 2231.
13. Mauthner .. *Ann.*, 1909, **370**, 374.

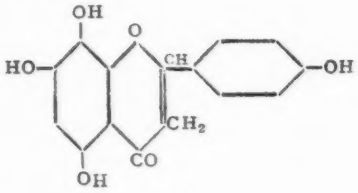
SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXV. Isomerisation of 5 : 7 : 8-Hydroxy Flavanones

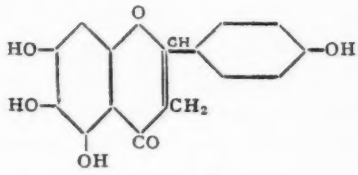
By Ishwar-Dass, N. Narasimhachari and T. R. Seshadri, F.A.Sc.
(From the Department of Chemistry, Delhi University)

Received November 21, 1952

Experiments using flavones and chromones have shown that 5:7:8-hydroxy or methoxy derivatives undergo isomeric change into the corresponding 5:6:7-substituted isomers when boiled with hydriodic acid (for a discussion see Mukerjee *et al.*).[1] The change is prevented when a substituent such as hydroxyl or phenyl is present in the 3-position.[2] This kind of isomeric change has not been studied in detail in the case of flavanones. It has however been recorded that carthamidin (5:7:8:4′-tetrahydroxy flavanone) (I) undergoes change into isocarthamidin (5:6:7:4′-tetrahydroxy flavanone) (II) even when heated with water in a sealed tube in the presence of animal charcoal.[3]



I

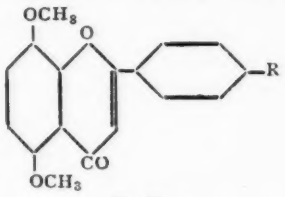


II

When dealing with the flavanones or the corresponding chalkones hydriodic acid cannot be used as a demethylating agent since it produces besides demethylation profuse decomposition which has not yet been understood. Aluminium chloride has been used successfully for partial as well as complete demethylation and with this reagent no isomeric change is brought about. Its action on methoxy flavanones is very similar to that on methoxy flavones. Regarding partial demethylation it has been used in nitrobenzene solution for the preferential demethylation of the 5-hydroxyl group of flavanones by Rao and Seshadri.[4] The synthesis of norwogonin (5:7:8-trihydroxyflavone) by the demethylation of its 5:8-dimethyl ether by Shah, Mehta and Wheeler[5] would indicate that the 8-methoxyl in flavanones can undergo easy removal. Its capacity to effect complete demethylation in

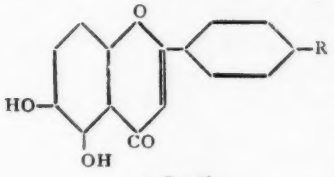
benzene solution without causing isomeric change has been employed for the synthesis of carthamidin and isocarthamidin.[6]

Hydrobromic acid has also been used for the demethylation of chalkones and flavanones. In this case the products are flavanones and the 7-methoxyl is invariably left out unaffected; this has been utilised for the convenient synthesis of sakuranetin and the 7-methyl ether of eriodictyol.[7] This reagent is known to cause isomerisation in the flavones, examples being the conversion of primetin dimethyl ether (III *a*) to 5: 6-dihydroxy flavone (IV *a*) and 5: 8: 4′-trimethoxy flavone (III *b*) to 5: 6: 4′-trihydroxy flavone (IV *b*).[8]



a, R = H
b, R = OCH_3

III

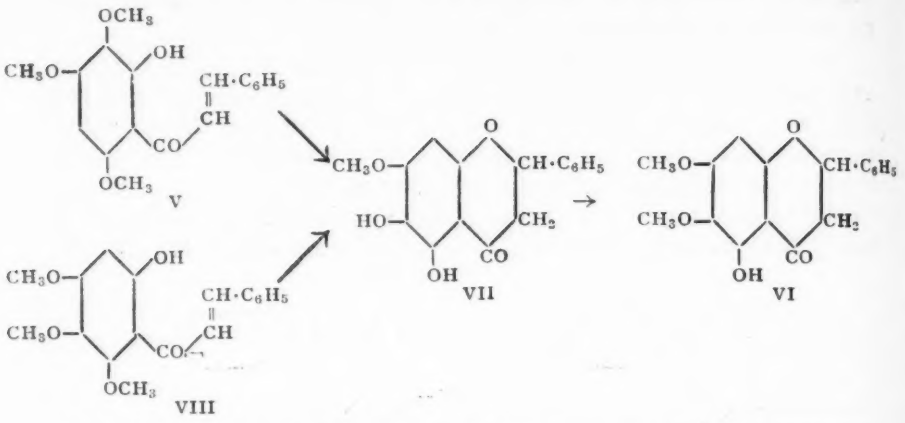


a, R = H
b, R = OH

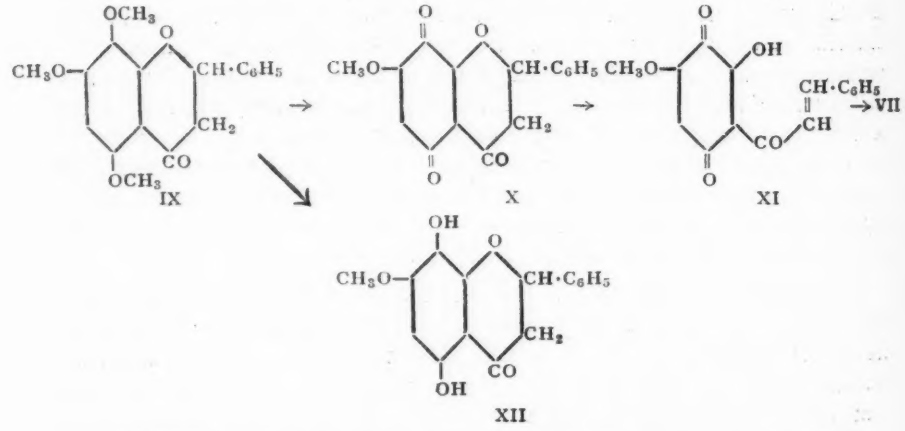
IV

For the purpose of the present study as the simplest suitable example 2-hydroxy-3: 4: 6-trimethoxy chalkone (V) has been employed. By the action of hydrobromic acid a product (A) is obtained which is a monomethyl ether and which does not give the reactions expected for 7-methoxy-5: 8-dihydroxy flavanone. On the other hand, it gives a green colour with ferric chloride changing to brown and does not react with *p*-benzoquinone. It would appear therefore that during the demethylation isomeric change has also taken place. The product could undergo partial methylation and form a dimethoxy compound (B) giving characteristic reactions for the presence of a 5-hydroxyl group. The constitution of (A) has been established by preparing 7-methoxy-5: 6-dihydroxy flavanone (VII) by the treatment of 2-hydroxy-4: 5: 6-trimethoxy chalkone (VIII) with hydrobromic acid; the constitution of B is then represented by VI.

In order to further confirm the constitution of the demethylation product (A) attempts have been made to prepare 7-methoxy-5: 8-dihydroxy flavanone adopting a different route. For this purpose 5: 7: 8-trimethoxy flavanone (IX) is subjected to oxidative demethylation with nitric acid[9] and 7-methoxy-5: 8-quinoflavanone (X) obtained. But when it is reduced using sodium hydrosulphite the product is again found to be identical with 7-methoxy-5: 6-dihydroxy flavanone (VII). These experiments indicate the readiness with which ring isomeric change takes place in the flavanone series in alkaline medium. It is interesting to note that the product is not a mixture



and the isomeric change is complete. In this connection may be mentioned the results of Rao and Seshadri[10] who reduced 2-hydroxy-4-methoxy-3: 6-quino-chalkone (XI) with sodium hydrosulphite and obtained 7-methoxy-5: 6-dihydroxy flavanone (VII) as the only product. These results are explicable on the basis that the conversion of the quinoflavanone to the corresponding quino-chalkone is quite easy and the *o*-hydroxyl group which is part of the quinol system is more reactive than the other.



7-Methoxy-5: 8-dihydroxy flavanone (XII) could however be successfully prepared by the demethylation of 5: 7: 8-trimethoxy flavanone (IX) using anhydrous aluminium chloride in nitrobenzene solution. This reagent has been used earlier in the demethylation of the 8-position of flavones.[5]

The product agreed in its properties with those of a 5: 8-dihydroxy compound. It dissolved readily in aqueous sodium carbonate, gave a green colour changing to deep red with ferric chloride and a positive *p*-benzoquinone reaction. It was different from the demethylation product (A) described earlier.

Experimental

7-Methoxy-5: 6-dihydroxy flavanone (VII):—

(A) *By the demethylation of 2-hydroxy-3: 4: 6-trimethoxy chalkone (V):*

2-Hydroxy-3: 4: 6-trimethoxy chalkone[9] (0·8 g.) was dissolved in glacial acetic acid (5 c.c.) and the solution treated with a saturated solution of hydrogen bromide in glacial acetic acid (8 c.c.). After leaving at room temperature for two hours it was heated on a boiling water-bath for one hour, then cooled and diluted with water (40 c.c.). The brown solid that separated was filtered, washed with water and crystallised from acetone-petroleum ether mixture. On recrystallising from methyl acetate it separated as pale yellow tiny prisms melting at 248–49° (decomp.). When the aqueous filtrate was neutralised with aqueous alkali it gave some more of the same product which was crystallised from methyl acetate. It gave a green colour with ferric chloride in alcoholic solution changing to brown with excess of the reagent. It developed no colour with *p*-benzoquinone in alcoholic solution (Found: C, 67·1; H, 4·5; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·2%). Yield 0·4 g.

Partial methylation (6: 7-dimethoxy-5-hydroxy flavanone) (VI).—The above dihydroxy flavanone (0·27 g.) was refluxed in acetone solution with dimethyl sulphate (0·11 c.c.) and anhydrous potassium carbonate (0·5 g.) for six hours. On filtering and distilling off acetone a pale yellow solid separated. It crystallised from acetone as pale yellow rectangular prisms melting at 230–32°. It gave a red colour with ferric chloride and was sparingly soluble in aqueous sodium hydroxide (Found: C, 67·5; H, 5·4; $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

(B) *By the demethylation of 2-hydroxy-4: 5: 6-trimethoxy chalkone (VIII).*—2-Hydroxy-4: 5: 6-trimethoxy chalkone[6] (1·0 g.) was demethylated with hydrobromic acid under exactly the same conditions as used in the previous experiment. On working up the product and crystallising first from acetone-petrol mixture and finally from methyl acetate it was obtained in the form of pale yellow tiny prisms melting at 248–49° (decomp.). It agreed in its properties with 7-methoxy 5: 6-dihydroxy flavanone described in experiment (A) and the mixed melting point was not depressed.

On partial methylation with 1 mole of dimethyl sulphate and potassium carbonate in dry acetone solution, the dihydroxy compound yielded a monomethyl ether which crystallised from alcohol as pale yellow rectangular prisms melting at 230–32°. It was identical with 5-hydroxy-6: 7-dimethoxy flavanone and the mixed melting point with the sample obtained in the previous experiment was undepressed.

7-Methoxy-5: 8-quinoflavanone (X):—

Nitric acid (10 c.c.; d, 1·2) was added to finely powdered 5: 7: 8-trimethoxy flavanone[6] (0·5 g.) cooled in ice water with shaking. During the course of five minutes the solid changed colour and slowly turned to a yellowish red semi-solid mass. The temperature was kept at 20° for 15 minutes and the clear supernatant liquid decanted. On adding ice-cold water to the semi-solid residue it solidified. It was filtered, washed repeatedly with water and dried. It crystallised from benzene as orange red long prismatic needles melting at 182–4°. It gave no colour with ferric chloride in alcoholic solution (Found: C, 67·8; H, 4·5; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

Reduction (5: 6-Dihydroxy-7-methoxy flavanone) (VII).—To a suspension of 7-methoxy-5: 8-quinoflavanone (0·2 g.) in water (10 c.c.) was added a solution of sodium hydrosulphite (2·0 g.) in water (10 c.c.) and the mixture boiled for 3 minutes. The original orange-red colour of the quinone changed to pale yellow. After cooling, the solid was filtered and washed with water. It crystallised from methyl acetate as pale yellow tiny prisms melting at 248–49° (decomp.). It gave a green colour with ferric chloride changing to brown with excess of the reagent. It was therefore identical in its reactions with 7-methoxy-5: 6-dihydroxy flavanone and mixed melting points with the two samples described earlier were undepressed.

In another experiment the same reduction was carried out with sodium hydrosulphite in presence of sodium carbonate with the same result.

7-Methoxy-5: 8-dihydroxy flavanone (XII):—

5: 7: 8-Trimethoxy flavanone[6] (0·6 g.) and anhydrous aluminium chloride (2·0 g.) were dissolved in dry nitrobenzene (10 c.c.) and the mixture refluxed over a water-bath for two hours. After allowing it to cool, petroleum ether was added to precipitate the complex. The supernatant liquid was decanted and the residue washed with petroleum ether repeatedly to remove nitrobenzene. The aluminium chloride complex was treated with ice and hydrochloric acid (20 c.c.). The last traces of nitrobenzene were removed by passing in steam. The pale-brown solid that separated was filtered and

washed with water. It was taken up in acetone and the dark coloured solution was treated with petroleum ether till there was turbidity which on allowing to stand cleared up depositing a sticky mass. The clear solution was decanted off, treated with more petrol and warmed to get a clear solution. The solvent was completely distilled off and the residue was crystallised from a mixture of absolute alcohol and petroleum ether from which it separated as pale yellow aggregates of stout prismatic needles melting at 133–4°. It gave a green colour with ferric chloride in alcoholic solution changing to deep red. It gave a red colour with *p*-benzoquinone in alcoholic solution. It dissolved completely in aqueous sodium carbonate (Found: C, 67·6; H, 4·6; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·2%).

Summary

Heating 2-hydroxy-3: 4: 6-trimethoxy-chalkone with hydrobromic acid yields instead of the expected 7-methoxy-5: 8-dihydroxy flavanone, the isomeric 7-methoxy-5: 6-dihydroxy flavanone. The same product is obtained by the partial demethylation of 2-hydroxy-4: 5: 6-trimethoxy chalkone. Attempts to prepare 5: 8-dihydroxy-7-methoxy flavanone by the reduction of the corresponding quinone again resulted in the formation of the isomeric 7-methoxy-5: 6-dihydroxy flavanone. The 5: 8-dihydroxy compound has been obtained by the partial demethylation of 5: 7: 8-trimethoxy flavanone by means of aluminium chloride in nitrobenzene solution.

References

1. Mukerjee *et al.* .. *Proc. Ind. Acad. Sci.*, 1953, **37A**, 127.
2. Seshadri *et al.* .. *Ibid.*, 1950, **32A**, 250.
   Narasimhachari *et al.* .. *Ibid.*, 1952, **35A**, 46.
3. Kuroda .. *J.C.S.*, 1930, 752.
4. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, 1946, **23A**, 213.
5. Shah, Mehta and Wheeler .. *J.C.S.*, 1938, 1555.
6. Sastri *et al.* .. *Proc. Ind. Acad. Sci.*, 1949. **29A**, 464.
7. Narasimhachari and Seshadri .. *Ibid.*, 1949, **29A**, 265; 1950, **32A**, 17.
8. Baker *et al.* .. *J.C.S.*, 1939, 1922; 1940, 1370.
9. Rao and Seshadri . *Proc. Ind. Acad. Sci.*, 1948, **27A**, 385.
10. ——— – .. *Ibid.*, 1952, **36A**, 130.

SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

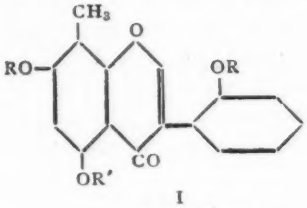
Part XXVI. A Synthesis of 8-Methyl Isogenistein

By T. R. Seshadri, F.A.Sc. and S. Varadarajan

(From the Department of Chemistry, University of Delhi, Delhi)

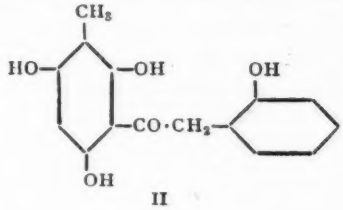
Received November 26, 1952

Among the crystalline products from soya beans Okano and Beppu[1] reported the isolation of the glycoside, 8-methyl isogenistin (sugar position unsettled) and its aglucone, 8-methyl isogenistein. The analytical values of the aglucone corresponded to the formula $C_{16}H_{12}O_5$. It was found to yield a dimethyl ether (I *b*), a trimethyl ether (I *c*) and a triacetate. On heating with alkali, it gave a tetrahydroxy ketone which was considered to have the structure, 2:4:6:2′-tetrahydroxy-3-methyl phenyl benzyl ketone (II) since it yielded C-methyl phloroglucinol (III *a*) and *o*-hydroxy phenyl acetic acid (IV *a*) on further degradation. The parent aglucone should therefore be 6- or 8-methyl-5:7:2′-trihydroxy isoflavone (I *a*). The location of the methyl group was determined by degradation of the trimethyl ether (I *c*) with alkali, when C-methyl phloroglucinol α-dimethyl ether (III *b*) and *o*-methoxy phenyl acetic acid (IV *b*) were obtained as the products. Hence Okano and

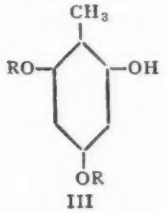


I

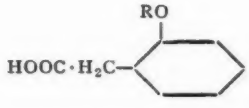
a, R = R′ = H
b, R = CH_3, R′ = H
c R = R′ = CH_3



II



III

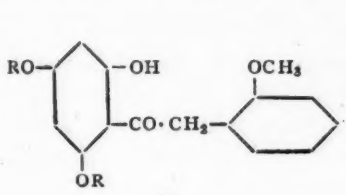


IV

a, R = H
b, R = CH_3

Beppu[1] assigned the structure of 8-methyl-5:7:2′-trihydroxy isoflavone (8-methyl isogenistein) (I *a*) to the natural compound.

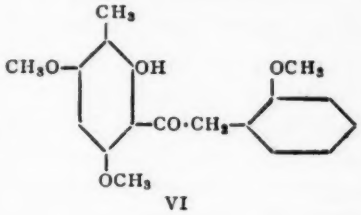
A synthesis of a compound of this structure (I *a*) has now been carried out along the lines of the synthesis of 8-methyl genistein, described in an earlier paper.[2] For this purpose, 2:4:6-trihydroxy-2′-methoxy phenyl benzyl ketone (V *a*) described in Part XXIV[3] is heated with excess of methyl iodide and potassium carbonate in acetone solution. The product is fractionally crystallised from alcohol. The less soluble fraction is 2-hydroxy-3-methyl-4:6:2′-trimethoxy phenyl benzyl ketone (VI). It does not give any blue or green colour with concentrated nitric acid[4] but gives a wine red ferric reaction. These properties are in agreement with this C-methyl formula. The more soluble fraction is identical with 2-hydroxy-4:6:2′-trimethoxy phenyl benzyl ketone (V *b*) described in an earlier publication.[3]



V

a, R=H

b, R=CH₃



VI

Condensation of 2-hydroxy-3-methyl-4:6:2′-trimethoxy phenyl benzyl ketone (VI) with ethyl formate and sodium[5] gives a good yield of 5:7:2′-trimethoxy-8-methyl isoflavone (I *c*).* This compound is found to melt at 178–79° and seems to be quite different from the trimethyl ether of the natural compound, whose melting point was reported as 152–53° by Okano and Beppu.[1] In this case also, as with 5:7:2′-trimethoxy isoflavone,[3] considerable difficulties exist in demethylation. When a mixture of acetic anhydride and hydriodic acid is employed for this purpose, a resinous product is obtained from which a small quantity of crystalline material melting at 230–32° could be isolated. The demethylation is more conveniently effected by aluminium chloride in benzene solution.[6] The product melts at 230–32° and is identical with the compound obtained by the demethylation of (I *c*) with hydriodic acid. Okano and Beppu[1] reported the melting point of the natural compound to be 300–02°. They have also mentioned that it gave a violet red colour with alcoholic ferric chloride. The deep green

* This compound has subsequently been found to be 2-hydroxy-5:7:2′-trimethoxy-8-methyl isoflavanone and has been converted into 5:7:2′-trimethoxy-8-methyl isoflavone, m.p. 183–84°.

colour given in this reaction by the synthetic substance in the present work is similar to the one given by the isomeric 8-methyl genistein[2] and is more in agreement with expectations for this structure than the violet red colour exhibited by the natural compound.

There is also considerable difference in the melting points of the acetates of the synthetic product and the natural compound of Okano and Beppu.[1] The latter has been reported to melt at 188° while the triacetate obtained in the present work becomes glassy at about 110° and melts at 120° completely showing that it is hydrated. These differences clearly establish that the natural compound cannot have the structure assigned to it by Okano and Beppu and similar to other compounds occurring along with it, it should also have a more complex structure (see Parts XXIII[2] and XXIV[3]).

EXPERIMENTAL

2-Hydroxy-3-methyl-4:6:2′-trimethoxy phenyl benzyl ketone (VI)

To a solution of 2:4:6-trihydroxy-2′-methoxy phenyl benzyl ketone (V *a*)[3] (5 g.) in acetone (150 c.c.), methyl iodide (10 c.c.) and potassium carbonate (20 g.) were added and the mixture refluxed for 4 hours. The potassium salts were filtered off and washed with acetone. After distilling off the solvent, water was added to the residue to dissolve potassium iodide. The precipitate was filtered and crystallised from alcohol four times when 2-hydroxy-3-methyl-4:6:2′-trimethoxy phenyl benzyl ketone was obtained in the form of thick colourless rectangular rods melting at 146–48°. Yield 0·65 g. It gave a wine red colour with alcoholic ferric chloride and was insoluble in aqueous sodium hydroxide (10%). It did not give a blue or green colour with concentrated nitric acid (Found: C, 68·0; H, 6·1; $C_{18}H_{20}O_5$ requires C, 68·4; H, 6·3%).

The alcoholic mother liquors on concentration yielded 2-hydroxy-4:6:2′-trimethoxy phenyl benzyl ketone (V *b*) which when recrystallised twice from alcohol separated as sheaves of colourless thin plates melting at 116–18° alone or when mixed with an authentic sample of the ketone described earlier.[3] Yield 3·0 g.

*5:7:2′-Trimethoxy-8-methyl isoflavone (I c)**

The above ketone (VI) (1 g.) was condensed with sodium (1 g.) and ethyl formate (25 c.c.) at 0°. After 48 hours in the refrigerator, ice and hydrochloric acid were added and the unreacted ester evaporated off. The precipitate was collected and crystallised from alcohol twice. 5:7:2′-Trimethoxy-8-methyl isoflavone separated as thick colourless prisms melting

* Please see footnote on an earlier page.

at 178–79°. Yield 0·75 g. (Found: C, 65·9; H, 5·7; $C_{19}H_{18}O_6$, H_2O requires C, 66·3; H, 5·8%). The water of crystallisation was not lost even on drying at 120° for 4 hours under reduced pressure.

5: 7: 2′-*Trihydroxy*-8-*methyl isoflavone* (8-*Methyl isogenistein*) (*I a*)

(i) The above trimethyl ether (0·5 g.) was suspended in benzene (200 c.c.) and well powdered anhydrous aluminium chloride (2·0 g.) was added and the mixture refluxed for 2 hours. Benzene was then distilled off and the residual aluminium chloride complex decomposed with ice and hydrochloric acid (10 c.c.). After 4 hours, the yellow precipitate of the trihydroxy isoflavone was collected and purified by dissolution in dilute sodium carbonate solution. The colourless precipitate obtained on acidification of the carbonate solution was crystallised twice from alcohol, when 8-methyl isogenistein separated as colourless tablets melting at 230–32° (decomp.). Yield 0·2 g. It gave a permanent deep green colour with alcoholic ferric chloride. (Found in a sample dried *in vacuo* at 120° for 6 hours: C, 67·8; H, 4·6; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

(ii) 5: 7: 2′-Trimethoxy-8-methyl isoflavone (0·9 g.) was dissolved in acetic anhydride (25 c.c.) and hydriodic acid (37 c.c., d., 1·7) was added carefully and the mixture refluxed for 2 hours at 140°, cooled and diluted with a saturated solution of sodium bisulphite (150 c.c.). The solution was neutralised by adding sodium bicarbonate. After 12 hours, the dark precipitate was collected, treated with dilute sodium carbonate solution and filtered. The filtrate on neutralisation gave the trihydroxy isoflavone, which when crystallised twice from dilute alcohol came out as colourless tablets melting at 230–32°. A mixed melting point with the sample obtained in (i) above was not depressed. Yield 90 mg.

5: 7: 2′-*Triacetoxy*-8-*methyl isoflavone*

The above trihydroxy isoflavone (0·2 g.) was acetylated with acetic anhydride and pyridine. The triacetate was crystallised thrice from alcohol. It was obtained as long colourless irregular prisms. It sintered at 110° and became glassy and melted at 118–20°. The melting point did not rise on further crystallisation (Found: C, 63·2; H, 4·9; $C_{22}H_{18}O_8$, $\frac{1}{2}H_2O$ requires C, 63·0; H, 4·5%).

The above acetate (0·15 g.) was deacetylated with a mixture of alcohol (7 c.c.) and concentrated hydrochloric acid (7 c.c.) by heating in a water-bath for 30 minutes. The solution was concentrated to 10 c.c., diluted with water and left overnight in the refrigerator. The precipitate was collected and crystallised from dilute alcohol. It melted at 230–32° and was identical with 5: 7: 2′-trihydroxy-8-methyl isoflavone.

SUMMARY

One of the crystalline compounds occurring in soya beans has been considered by Okano and Beppu to be 8-methyl isogenistein and this structure was based on the alkali degradation of the compound and its trimethyl ether. A compound of this structure is now synthesised starting from 2:4:6-trihydroxy-2′-methoxy phenyl benzyl ketone, along the lines of synthesis of 8-methyl genistein described in Part XXII. Here also the products are found to be different from those reported by Okano and Beppu and the natural compound should therefore have a more complex structure.

REFERENCES

1. Okano and Beppu .. *J. Agri. Chem. Soc. Japan*, 1939, **15**, 645.
2. Seshadri and Varadarajan .. *Proc. Ind. Acad. Sci.*, 1953, **37A**, 145 and 508.
3. ——— ——— .. *Ibid.*, 1953, **37A**, 514.
4. Rao and Seshadri .. *Ibid.*, 1949, **30A**, 30.
5. Venkataraman *et al.* .. *J.C.S.*, 1934, 513 and 1770.
6. Seshadri *et al.* .. *Proc. Ind. Acad. Sci.*, 1947, **24A**, 213; 1947, **25A**, 432; 1949, **29A**, 72; 1952, **35A**, 34, 82 and 202.

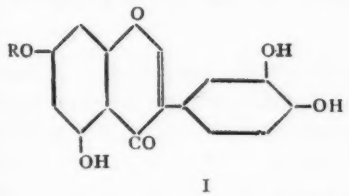
SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XXVII. A Note on the Synthesis of Santal

By N. Narasimhachari and T. R. Seshadri, F.A.Sc.
(*From the Department of Chemistry, University of Delhi*)

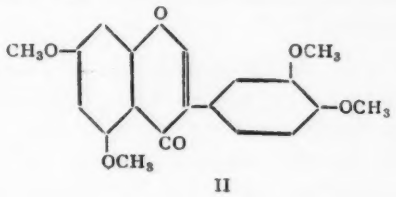
Received December 18, 1952

In our earlier publication[1] was reported the synthesis of santal (I *a*) by two methods, (1) in a fair yield by the hydriodic acid demethylation of santal trimethyl ether (5 : 7 : 3′ : 4′-tetramethoxy isoflavone) (II), and (2) in a rather poor yield by the partial methylation of norsantal (I *b*) just analogous to the earlier synthesis of prunetin.[1a] Iyer *et al.*[2] reported another synthesis from 5 : 7-dimethoxy-3′ : 4′-methylenedioxy isoflavone which by demethylenation and partial demethylation using anhydrous aluminium bromide yielded santal. This seems to have been based on the assumption that demethylation of methoxyl groups in the side-phenyl nucleus of the isoflavone structure is not possible without affecting the methoxyl in the 7-position. The earlier synthesis mentioned above indicated that this assumption is not valid. In our subsequent papers[3,4] an explanation for the resistance to demethylation of the 7-methoxyl was given and conditions for the satisfactory production of the 7-methyl ethers of isoflavones in good yields by demethylating the fully methylated compounds using hydriodic acid were worked out. By this method isoformononetin (III *a*)[3] and prunetin (IV *a*)[4] were prepared in quantitative yields from daidzein dimethyl ether (III *b*) and genistein trimethyl ether (IV *b*) respectively. However this convenient method has not been used earlier for the synthetic preparation of santal. The partial demethylation of santal trimethyl ether has now been carried out using the modified conditions and the product is found to be exclusively santal obtained in

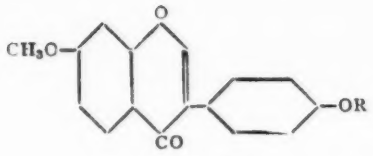


I

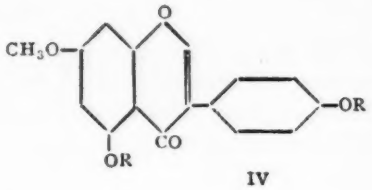
a, R = CH_3
b, R = H



II



III



IV

a, R = H
b, R = CH_3

almost quantitative yield. Thus this method of partial demethylation is the most convenient for the preparation of this naturally occurring isoflavone.

As already mentioned[1] the alternative method of preparation involving partial methylation of nor-santal (I *b*) is of biogenetic significance. The preparation has now been repeated using larger quantities; and santal and its acetate obtained in this way have been compared with samples obtained by the method of demethylation and found to be identical.

EXPERIMENTAL

Santal

1. *By partial demethylation.*—5 : 7 : 3′ : 4′-Tetramethoxy isoflavone (1 g.) was dissolved in acetic anhydride (3 c.c.) and the solution treated with hydriodic acid (10 c.c.; sp. gr. 1·7) while cooling under the tap. The mixture was heated in an oil-bath at 115–20° for half an hour. It was then cooled and diluted with sulphurous acid. The pale yellow solid that separated was filtered, washed with water and then with aqueous sodium carbonate (1%) in which it was almost insoluble. After finally washing with water and drying in air it was crystallised from ethyl acetate from which it separated as colourless rectangular plates and prisms and melted at 220–22°.[5] It gave an intense brownish red colour with ferric chloride (Found: C, 60·8; H, 4·4; $C_{16}H_{12}O_6$, H_2O requires C, 60·4; H, 4·4%).

The triacetate crystallised from ethyl acetate as colourless clusters of needles melting at 168–70° and was identical with the product described earlier.[1, 5]

2. *Partial methylation.*—On repeating the partial methylation of nor-santal (1·5 g.) using 1 mole of dimethyl sulphate and working up the product as already described[1] santal (0·25 g.) was obtained. It gave on acetylation the triacetate which crystallised from ethyl acetate as clusters of colourless needles melting at 168–70° and was identical with the acetate described in the above experiment; a mixed melting point with that sample was undepressed (Found: C, 61·9; H, 4·4; $C_{22}H_{18}O_9$ requires C, 62·0; H. 4·2%).

Summary

The partial demethylation of 5:7:3':4'-tetramethoxy isoflavone has now been effected under improved conditions and an almost quantitative yield of santal obtained. Partial methylation of nor-santal has been repeated using larger quantities and santal and its acetate prepared and studied.

References

1. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1950, **32A**, 342.
1*a*. ———— .. *Ibid.*, 1950, **32A**, 256.
2. Iyer *et al.* .. *Ibid.*, 1951, **33A**, 228.
3. Aghoramurty *et al.* .. *Ibid.*, 1951, **33A**, 251.
4. Narasimhachari *et al.* .. *Ibid.*, 1952, **36A**, 194.
5. Robertson *et al.* .. *J.C.S.*, 1949, 1571.

EXPERIMENTS ON THE SYNTHESIS OF COUMARYL STYRENES

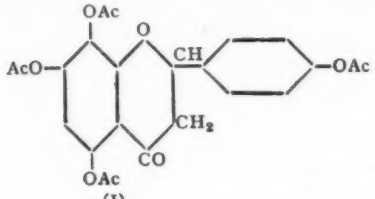
By (Miss) L. Ponniah and T. R. Seshadri, F.A.Sc.

(*From the Department of Chemistry, Delhi University*)

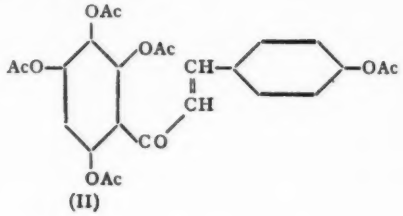
Received October 14, 1952

Several hydroxy and methoxy stilbenes are found to occur in nature, particularly in the heartwoods of plants. Further, some stilbene derivatives have recently come into prominence for their marked physiological properties; *e.g.*, stilbamidine is a well-known drug for the treatment of trypanosome infections and stilbœstrol is a successful synthetic œstrogen. Coumaryl styrenes resemble stilbene derivatives in view of the aromatic characteristics exhibited by the pyrone ring. Certain coumaryl styrene derivatives were needed in connection with an investigation on insecticides and fish poisons. Besides these, there was another interest in the preparation of coumaryl styrenes. In the course of her work on the constitution of carthamidin, Kuroda[1] was able to isolate besides the normal flavanone tetra-acetate (α) (I), and the chalkone penta-acetate (β) (II), a third acetate by high temperature acetylation, which she designated γ-acetate and formulated as a coumaryl styrene (III).

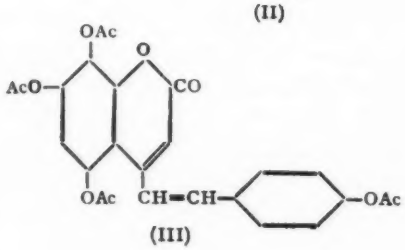
This was based on the assumption that the chalkone structure of the β-acetate underwent further transformation analogous to Perkin's reaction producing a coumarin structure. But, no other evidence was provided in support, except analysis for carbon and hydrogen.



(I)

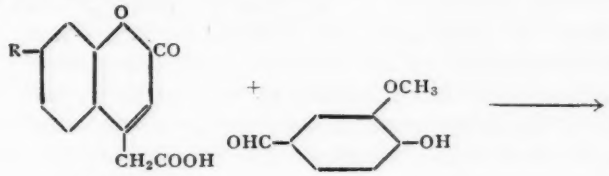


(II)

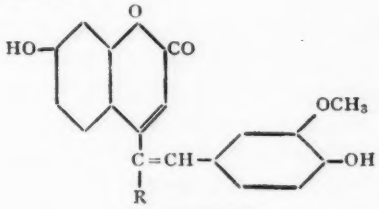


(III)

For the preparation of coumaryl styrenes, Dey and Row[2] utilised the reactivity of the methylene group in coumarin-4-acetic acids such as (IV) and condensed them with aromatic aldehydes in the presence of piperidine, whereby coumaryl styrenes were obtained.

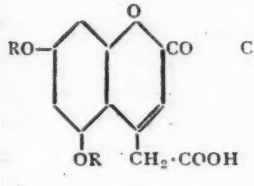


IV, R=CH_3
VII, R=OH

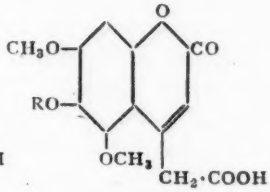


V, R=CO_2H
VI, R=H

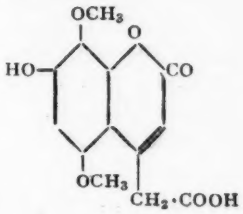
To serve our purpose, the following coumarin-acetic acids were prepared adopting the general method of Dey and Row[2] which consists in condensing the respective phenols with acetone dicarboxylic acid: 7-Hydroxy coumarin-4-acetic acid (VII), 5: 7-dihydroxy coumarin-4-acetic acid (VIII), 5: 7-dimethoxy coumarin-4-acetic acid (IX), 5: 7-dimethoxy-6-hydroxy coumarin-4-acetic acid (X), 5: 6: 7-trimethoxy coumarin-4-acetic acid (XI) and 5: 8-dimethoxy-7-hydroxy coumarin-4-acetic acid (XII).



VIII, R=H
IX, R=CH_3



X, R=H
XI, R=CH_3



XII

Compounds (VII) and (VIII) are already known.[3] For the preparation of 5: 7-dimethoxy-coumarin-4-acetic acid (IX), the methylation of the corresponding dihydroxy compound does not lead to good results. The difficulty seems to be related in some way with the presence of the 5-hydroxyl group.

The direct condensation of O-dimethyl phloroglucinol with acetone dicarboxylic acid works smoothly and gives much better yields. On the other hand, 6-hydroxy-5 : 7-dimethoxy-coumarin-4-acetic acid (X) obtained from 2 : 6-dimethoxy quinol undergoes methylation quite satisfactorily, and the trimethoxy coumarin acetic acid (XI) could be obtained in good yield. For the preparation of 5 : 8-dimethoxy-7-hydroxy coumarin-4-acetic acid (XII), it has not been found to be necessary to use 2 : 5-dimethoxy resorcinol. Its dibenzyl ether, an earlier intermediate in its preparation, could be directly employed. If the temperature of the reaction mixture, during the condensation, is kept between 10° and 12° and not allowed to go too low, the coumarin condensation is accompanied by debenzylation giving the required hydroxycoumarin acetic acid.

Of these, 7-hydroxycoumarin-4-acetic acid undergoes condensation with benzaldehyde and vanillin, giving rise to the corresponding coumaryl styrenes. There is considerable decomposition of the acid during this reaction giving rise to the simultaneous formation of 4-methyl umbelliferone which has to be removed by repeated fractional crystallisation. The products have all the properties of coumaryl styrenes. Particularly characteristic is the colour reaction in alkaline solutions exhibited by the 4′-hydroxy compound. The other coumarin acetic acids do not undergo condensation with aromatic aldehydes, but they suffer decomposition yielding the corresponding 4-methyl coumarins. To avoid this, the Knœvenagel condensation has been tried at temperatures lower than 120°; but the components do not react. Protection of the carboxylic group by esterification also leads to inactivity. Hence, this method of preparing coumaryl styrenes is of limited applicability and other alternative methods are being explored.

Meanwhile, some experimental work has been carried out to test the validity of the suggestion of Kuroda[1] regarding the constitution of γ-acetates, using simpler and more easily available flavanones and chalkones. 7-Hydroxy flavanone and 2 : 4-dihydroxy chalkone have been subjected to acetylation under various conditions. With acetic anhydride and sodium acetate at 100° both yield as the main product 7-acetoxy flavanone (m.p. 104°). The diacetate of the chalkone could be obtained as a liquid by treatment of the dihydroxy chalkone with acetyl chloride and pyridine. Both these acetates do not give any colour with ferric chloride.

The above 7-hydroxy flavanone and dihydroxy chalkone were heated with sodium acetate and acetic anhydride at 180° using conditions approximating as closely as possible to Perkin's reaction, in order to get exclusively the γ-acetate. Both yield as the main product a substance melting at 118°.

Its composition agrees with the expectations for a coumaryl styrene structure, but its properties do not agree with 7-acetoxy-coumaryl styrene. Not only are the melting points widely different, but on deacetylation with alcoholic hydrochloric acid, the γ-acetate yields a colourless product which melts with decomposition at about 128°, does not give colour with ferric chloride and dissolves in sodium hydroxide giving a colourless solution. 7-Hydroxy coumaryl styrene melts much higher; it is yellow and gives an orange coloured solution with alkali.

2-Hydroxy-4-methoxy chalkone, when acetylated at 180° with sodium acetate and acetic anhydride yields a product, which should be considered to be the chalkone acetate (β-acetate). This behaviour is markedly different from that of the hydroxy compound. The nature of the product is clear, not only from its composition, but also from its hydrolysis giving rise to the original chalkone. This would indicate that a γ-acetate is not invariably formed when high temperatures are employed for the acetylation.

As a more suitable example for verifying Kuroda's suggestion, the acetylation of naringenin has been examined next. In this case, the α- and β-acetates have been prepared earlier by Asahina.[4] The first was obtained by him by boiling naringenin with acetic anhydride and a drop of concentrated sulphuric acid and its melting point was recorded as 55–56°. A more convenient method[5] adopted in this laboratory is to use acetyl chloride and pyridine in the cold and the melting point has been found to be higher (80°). The β-acetate was obtained by Asahina *et al.* by heating naringenin with acetic anhydride and sodium acetate. Its melting point has been recorded as 133–36°. A third acetate has now been obtained by acetylation of naringenin with acetic anhydride and sodium acetate at 180°. It is very sparingly soluble in solvents and melts at 193°. These and its composition agree with the expectations for a γ-acetate. For reasons already explained, the required styrene derivative (5:7:4′-triacetoxy coumaryl styrene) could not be prepared for comparison. But the reactions of the γ-acetate show definitely that it is not a coumaryl styrene derivative. Deacetylation with alcoholic hydrochloric acid yields a product which is colourless, does not give ferric chloride reaction and forms a pale yellow solution in alkali. On the other hand, coumaryl styrenes having hydroxyl groups, particularly one in the 4′-position, are yellow in colour and give bright colours with dilute alkali.

From the results described in the above paragraphs, it should be concluded that the γ-acetates are not coumaryl styrene derivatives and their mode of formation cannot be as suggested by Kuroda. Among other possibilities, they could not have the simple chalkone or flavanone skeletons because the product of deacetylation from naringenin γ-acetate does not

give any ferric chloride colour. This should be observed if it were a 2-hydroxy chalkone or a 5-hydroxy flavanone.

EXPERIMENTAL

7-Hydroxy coumaryl styrene

7-Hydroxy coumarin-4-acetic acid[3] (6 g.) was mixed with benzaldehyde (3·5 g.), piperidine (10 drops) was added and the mixture heated under air reflux at 130–35° in an oil-bath for 4 hours. The resulting dark red sticky mass was extracted with hot alcohol; the alcoholic solution on standing for a week deposited an yellow crystalline mass of the styrene which was filtered off and recrystallised from methyl alcohol, when fine needles were obtained. The yield was 1·5 g. The styrene melted at 213–14°, dissolved readily in aqueous sodium carbonate, and gave no colour with ferric chloride in alcohol. It dissolved in 10% sodium hydroxide to form an orange solution which on standing or when warmed in a water-bath at 70° for a minute became colourless and on acidification gave the original substance (Found: C, 77·7; H, 5·1. $C_{17}H_{12}O_3$ requires C, 77·3; H, 5·4%).

7-Acetoxy-coumaryl styrene

7-Hydroxy coumaryl styrene (0·5 g.) was heated with acetic anhydride (5 c.c.) and fused sodium acetate (1 g.) in an oil-bath at 100° for an hour. The product crystallised from dilute alcohol as colourless needles (0·4 g.) melting at 198° (Found: C, 74·6; H, 4·7. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·5%).

7-Methoxy-coumaryl styrene

7-Hydroxy coumaryl styrene (0·5 g.) was dissolved in dry acetone (20 c.c.), anhydrous potassium carbonate (3 g.) and dimethyl sulphate (0·3 c.c.) were added and the mixture refluxed for 6 hours. The acetone solution was filtered and evaporated whereby a colourless semi-solid was obtained. It solidified in contact with alcohol and on crystallisation from alcohol gave colourless needles having a pale yellow tinge and melting at 149–51° (Found: C, 78·2; H, 5·4. $C_{18}H_{14}O_3$ requires C, 77·7; H. 5·0%).

7: 4′-Dihydroxy-3′-methoxy-coumaryl styrene (VI)

7-Hydroxy coumarin-4-acetic acid (4·8 g.) and vanillin (3·3 g.) were mixed with piperidine (10 drops) and the mixture refluxed in an oil-bath, the temperature of which was gradually raised to 130–35°. Raising the temperature rapidly causes profuse decomposition of the coumarin-4-acetic acid into 4-methyl umbelliferone. After 3·5 hours the deep red reaction mixture was allowed to cool, when an yellow viscous product was obtained. It was

macerated with a small quantity of alcohol and left in the refrigerator when it solidified to an yellow amorphous solid. It was subjected to repeated fractional crystallisation from alcohol. The more sparingly soluble portion was collected and crystallised from absolute methyl alcohol, when yellow rectangular plates melting at 218° were obtained. It dissolved in aqueous sodium bicarbonate with difficulty but was readily soluble in aqueous sodium carbonate. It formed a bright red solution in aqueous sodium hydroxide, but the solution became colourless on standing or when warmed in a water-bath for a short time (Found: C, 67·4; H, 5·0. $C_{13}H_{14}O_5$, $\frac{1}{2}H_2O$ requires C, 67·7; H, 4·7%).

5: 7-*Dimethoxy-coumarin*-4-*acetic acid* (IX)

(i) 5: 7-Dihydroxycoumarin-4-acetic acid[3] (3·5 g.) obtained from phloroglucinol and acetone dicarboxylic acid was methylated by boiling with dimethyl sulphate (5·5 c.c. excess) and potassium carbonate (30 g.) in dry acetone (120 c.c.) for 6 hours. When the mixture was filtered and the filtrate evaporated 5: 7-dimethoxy-coumarin-4-acetic acid methyl ester separated out as a pale pink amorphous solid. On re-crystallisation, a colourless product melting between 120° and 130° was obtained. It was found to be mixed with 5: 7-dimethoxy-4-methyl coumarin from which it could not be separated. However, after boiling with 10% sodium carbonate for an hour (hydrolysis), filtration and acidification of the carbonate solution, 5: 7-dimethoxy coumarin-4-acetic acid was obtained. It was purified by dissolution in aqueous sodium carbonate and reprecipitation with hydrochloric acid. It then melted with decomposition at 177°.

(ii) O-Dimethyl phloroglucinol[6] (12·5 g.) was condensed in the usual way with acetone dicarboxylic acid from 24 g. of citric acid, keeping the temperature of the reaction strictly below 5°. The product (8 g.) was quite pure and first melted at 205° with decomposition, but on boiling with alcohol in which it was very sparingly soluble, it got converted into the stable form which melted at 177° (decomp.) (Found: C, 59·2; H, 5·0. $C_{13}H_{12}O_6$ requires C, 59·1; H, 5·0%).

5: 7-*Dimethoxy*-6-*hydroxy coumarin*-4-*acetic acid* (*X*)

2: 6-Dimethoxy quinol[7] (8 g.) was condensed in the usual way[2] with acetone dicarboxylic acid (from 11·5 g. of citric acid) when 5: 7-dimethoxy-6-hydroxy coumarin 4-acetic acid (6·2 g.) melting at 234° was obtained. The acid dissolved in aqueous sodium carbonate to give an yellow solution with green fluorescence. On recrystallisation from alcohol, extremely long silky needles of the stable form of the acid melting at 200° (decomp.) were obtained (Found: C, 56·0; H, 4·6. $C_{13}H_{12}O_7$ requires C, 55·7; H, 5·0%).

5:6:7-*Trimethoxy-coumarin-4-acetic acid methyl ester*

5:7-Dimethoxy-6-hydroxycoumarin-4-acetic acid (2·1 g.) was suspended in dry acetone (250 c.c.), anhydrous potassium carbonate (20 g.) and dimethyl sulphate (4 c.c.) were added and the mixture refluxed for 30 hours. The potassium salts were filtered off and the acetone solution concentrated. The solid left behind (1·8 g.) was crystallised from acetone when colourless needles melting at 140–41° were obtained. It was insoluble in aqueous sodium carbonate as well as in sodium hydroxide, sparingly soluble in alcohol and readily soluble in acetone (Found: C, 58·5; H, 4·5. $C_{15}H_{16}O_7$ requires C, 58·4; H, 4·5%).

5:6:7-*Trimethoxy-coumarin-4-acetic acid* (*XI*)

The above ester (1·8 g.) was dissolved in the minimum quantity of alcohol, 10% sodium carbonate solution (40 c.c.) was added to it and then heated on a steam-bath. After half an hour the ester was found to remain unchanged and hence 10% sodium hydroxide solution (20 c.c.) was added and the heating continued for a further half hour. The solution was then filtered from a small quantity of insoluble material and then cooled in ice and acidified. The crude product on crystallisation from alcohol gave long stout needles melting at 177° (decomp.). It dissolved in aqueous sodium carbonate without any fluorescence. It was readily soluble in alcohol and moderately soluble in acetone and chloroform (Found: C, 53·4; H, 4·7. $C_{14}H_{14}O_7$, H_2O requires C, 53·8; H, 5·1%).

5:8-*Dimethoxy-7-hydroxycoumarin-4-acetic acid* (*XII*)

2:6-Dibenzyloxy-1:4-dimethoxy benzene[8] (8 g.) was condensed with acetone dicarboxylic acid (from 5·5 g. of citric acid) keeping the temperature of the reaction between 10° and 12°. If the temperature was kept low, debenzylation did not take place effectively, the product became pasty and the yield was considerably reduced. The maximum yield realised was 3·5 g. The product on crystallisation from alcohol gave rectangular plates melting with decomposition at 198° (Found: C, 52·6; H, 4·6. $C_{19}H_{12}O_7$, H_2O requires C, 52·3; H, 4·7%).

γ-Acetate of 7-hydroxy flavanone

7-Hydroxy flavanone (0·6 g.) was suspended in acetic anhydride (9 c.c.), fused sodium acetate (0·7 g.) added and the mixture heated under air reflux in an oil-bath at 180° for 8 hours. It was allowed to cool and the excess of acetic anhydride decomposed in the usual way by adding crushed ice to the reaction mixture. After allowing it to stand overnight, the precipitated acetate was filtered off and repeatedly crystallised from a mixture of one

part of ethyl acetate and four parts of petroleum ether. The yield was very poor, 50 m.g., m.p. 118°. The product on recrystallisation from alcohol gave clusters of colourless needles melting at 119–20° (Found: C, 70·5; H, 6·0; loss on drying *in vacuo* at 110°, 5·9%. 7-Acetoxy coumaryl styrene formula: $C_{19}H_{14}O_4$, H_2O requires C, 70·3; H, 4·9; H_2O loss, 5·6%).

Acetylation of 2: 4-*dihydroxy chalkone at elevated temperatures*

2: 4-Dihydroxy chalkone (1 g.) was suspended in acetic anhydride (10 c.c.), fused sodium acetate (2 g.) added and the mixture refluxed for 8 hours at 180° in an oil-bath. The product was worked up in the usual way, and crystallised from a mixture of ethyl acetate and petroleum ether. It melted at the same temperature as the γ-acetate of 7-hydroxy flavanone (118°–19°) and the mixed m.p. was undepressed. It gave no colour with ferric chloride in alcohol solution.

Acetylation of 2: 4-*dihydroxy chalkone at lower temperatures*

(i) 7-*Acetoxy flavanone.*—2: 4-Dihydroxy chalkone (0·5 g.), fused sodium acetate (1 g.) and acetic anhydride (5 c.c.) were mixed together and heated under air reflux at 100–10° in an oil-bath for 2 hours. The product when worked up in the usual way, yielded a colourless substance having a pale yellow tinge and melting at 96–98°. The yield was quantitative. When crystallised from alcohol glistening long needles melting at 104–05° were obtained. The substance was found to be identical with 7-acetoxy flavanone (see Ellison,[9] m.p. 98°).

(ii) *Chalkone diacetate.*—2: 4-Dihydroxy chalkone, acetic anhydride and fused sodium acetate were mixed in the same proportions as above and heated at 125–30° in an oil-bath for 5 hours. After cooling, acetic anhydride was removed under reduced pressure, the acetate taken up in ethyl acetate and petroleum ether was added until turbidity appeared. It was allowed to stand for a short time and then filtered and concentrated. The acetate was obtained as a viscous oil and it gave no colour with ferric chloride. In contact with water, it was found to undergo hydrolysis giving positive colour test with alcoholic ferric chloride.

(iii) 2: 4-Dihydroxy chalkone (1 g.) was acetylated in the cold, with acetyl chloride (0·72 c.c.) and pyridine (7 c.c.). The resulting product was taken up in ethyl acetate and the ethyl acetate solution washed repeatedly with ice-cold 1% hydrochloric acid to remove the pyridine and once with ice-cold sodium bicarbonate solution. It was again washed with cold water, the solution dried over sodium sulphate and the solvent finally distilled off.

The resulting oily product did not solidify even on keeping in the refrigerator for a long time.

Acetylation of 2-hydroxy-4-methoxy chalkone: *2-Acetoxy-4-methoxy chalkone*

2-Hydroxy-4-methoxy chalkone (1 g.) was heated with acetic anhydride (10 c.c.) and fused sodium acetate (2 g.) at 180° in an oil-bath for 8 hours. It was allowed to cool, and crushed ice was added to the reaction mixture and the precipitated sticky mass of the acetate was purified by repeated crystallisation from ethyl acetate and petroleum ether mixture, when colourless rectangular prisms (150 mg.) melting at 66-68° were obtained (Found: C, 73·6; H, 5·9; $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%). When deacetylated with aqueous alcoholic hydrochloric acid it yielded the original chalkone.

γ-Acetate of naringenin

Naringenin (1 g.) was suspended in acetic anhydride (10 c.c.), fused sodium acetate (2 g.) added and the mixture heated under air reflux in an oil-bath at 180° for 8 hours. After cooling, the mixture was treated with crushed ice and allowed to stand in order to decompose the excess of acetic anhydride. The precipitated solid was crystallised from a large volume of alcohol when colourless glistening needles were obtained; m.p. 192–93°. Yield, 0·2 g. (Found: C, 64·9; H, 4·6. Calculated for 5:7:4′-triacetoxy coumaryl styrene formula: $C_{23}H_{18}O_8$. C, 65·4; H, 4·2%). The acetate was dissolved in hot alcohol and an equal volume of hot concentrated hydrochloric acid was added, when a lemon yellow colour was produced, which disappeared after two minutes. The mixture was boiled for 15 minutes (even a longer period, 2 hours gave the same result) in a water-bath, allowed to cool, diluted with water and extracted with ether. On removal of ether, a colourless product melting at 270–74° separated out. Recrystallisation from alcohol yielded colourless plates melting with decomposition at 274–5°. The substance was very soluble in alcohol and gave no colour with ferric chloride and dissolved in aqueous sodium hydroxide to form a pale yellow solution. It did not give a positive reaction with magnesium and hydrochloric acid for a flavanone (Found: C, 64·2; H, 4·9; loss on drying *in vacuo* at 120° for 10 hours, 5·6%. Coumaryl styrene structure, $C_{17}H_{12}O_5$, H_2O requires C, 64·9; H, 4·5. Water loss, 5·7%).

Summary

A number of hydroxy and methoxy coumarin acetic acids have been prepared by the method of Dey and Row with a view to convert them into the corresponding coumaryl styrenes. Except the simplest of them, *i.e.*, 7-hydroxy coumarin-4-acetic acid, the others do not undergo the condensation with aromatic aldehydes, but suffer only decarboxylation. A study of

the γ-acetates obtained by the high temperature acetylation of simpler chalkones and flavanones indicates that they are not coumaryl styrene derivatives, though their compositions agree with such.

References

1. Kuroda .. *J.C.S.*, 1930, 752.
2. Dey & Row .. *J.I.C S.*, 1924–25, **1**, 111 and 278.
3. Dey .. *J.C.S.*, 1915, 1606.
4. Asahina and Inubuse .. *Ber.*, 1928, **61**, 1514.
5. Bannerjee and Seshadri .. *Proc. Ind. Acad. Sci.*, 1952, **36A**, 134.
6. Pratt and Robinson .. *J.C.S.*, 1924, 193.
7. Baker .. *Ibid.*, 1941, 605.
8. Baxter *et al.* .. *Ibid.*, 1949, S 31.
9. Ellison .. *J.C.S.*, 1927, 1727.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

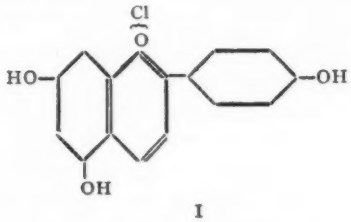
Part XLII. A Synthesis of 6-Hydroxy Pyrylium Salts of the Gesneridin Type

By (Miss) L. Ponniah and T. R. Seshadri, F.A.Sc.

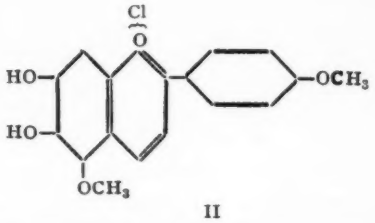
(From the Department of Chemistry, Delhi University)

Received September 29, 1952

The widely occurring and important anthocyanidins are pyrylium salts related to the flavonols, and have a hydroxyl in the 3-position. Members belonging to the flavone type are rare, gesneridin (I) and carajuridin (II) being the only two representatives of this group occurring in nature. The former is found as its glucoside 'gesnerin' in the orange coloured flowers of *Gesnera fulgens*, whereas the latter was discovered as its colour base 'carajurin' in the rare cosmetic pigment 'carajura' which is considered to originate from an anthocyanin similar to gesnerin. In fact, carajuridin is the 5:4′-dimethyl ether of carajuretin having the constitution of 6-hydroxy gesneridin.



I

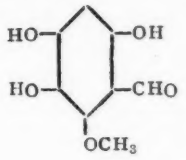


II

The synthesis of gesneridin[1] was accomplished by the condensation of O-benzoyl phloroglucinaldehyde with *p*-methoxy acetophenone, and by the subsequent debenzoylation and demethylation of the intermediate product. But, the synthesis of carajuridin has been proved to be very difficult, and has not been accomplished so far. However, in the course of the investigation on the constitution of carajuridin, the synthesis of a number of 6-hydroxy pyrylium salts of the gesneridin type was achieved by Chapman, Perkin and Robinson.[2] They condensed antiarol aldehyde with *p*-methoxy acetophenone and obtained 5:6:7:4′-tetramethoxy flavylium chloride which they demethylated to carajuretin chloride. Further, the condensation of iretol and 2:6-dimethoxy quinol was carried out with anisoyl acetone to obtain 5:7-dihydroxy-6:4′-dimethoxy-4-methyl flavylium chloride and

5:7:4′-trimethoxy-6-hydroxy-4-methyl flavylium chloride respectively. Both were demethylated to give the corresponding hydroxy compounds. Even earlier, 2-hydroxy-5-methoxy benzaldehyde was condensed with *p*-methoxy acetophenone and acetoveratrone, and the products demethylated.[3]

The main difficulty in the synthesis of carajurin lies in the presence in the molecule of a hydroxyl group in the 6-position along with a methoxyl in the 5-position. In general, the synthesis of partial methyl ethers offers some difficulty, but carajurin represents the only example, where the difficulties have not yet been surmounted. Methods of partial methylation and demethylation, which have been so very successful in the synthesis of partial methyl ethers of anthoxanthins, have not been shown to be possible in the case of anthocyanidins. Direct synthesis, using the required aldehyde and ketone components, seems to be the only available method, with the exception of benzoylation and benzylation, which could be employed for the temporary protection of certain reactive hydroxyl groups of the aldehyde component. For the synthesis of carajurin, there was need therefore to work out a satisfactory method of preparing 2:4:5-trihydroxy-6-methoxy benzaldehyde (III), or a suitable derivative of it, and also the most satisfactory conditions for effecting its condensation with *p*-methoxy acetophenone.

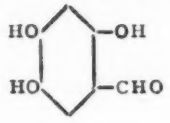


III

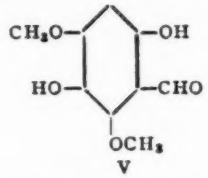
As part of exploratory work, a synthesis of simpler 6-hydroxy pyrylium salts of the 'gesneridin' type has now been carried out. Since nuclear oxidation with persulphate of monomethyl phloroglucinaldehyde was expected to provide the most convenient method of obtaining aldehyde (III), this method has been used for obtaining the simpler aldehydes required in the preliminary work. No detailed investigation of the application of this method for the preparation of polyhydroxy benzaldehydes seems to have been made before.

Gentisic aldehyde[4] and 2:5-dihydroxy-3-methoxy benzaldehyde[5] have already been prepared from salicylaldehyde and ortho-vanillin respectively, by persulphate oxidation. In a similar way, the otherwise tedious preparation of hydroxy-quinol aldehyde (IV) has now been made easy, by the oxidation of the readily accessible β-resorcylaldehyde. Though the yield is not good, the simplicity of the method more than provides compensation, and

it is quite suitable for the ready preparation of small amounts of the aldehyde. Further, 2: 6-dimethoxy quinol aldehyde (V) has now been prepared from 4: 6-O-dimethyl phloroglucinaldehyde. These are condensed with *p*-hydroxy and *p*-methoxy acetophenones, the two ketones needed for the synthesis of pyrylium salts related to gesneridin and carajuridin.



IV



V

In a polyhydroxy aldehyde, the reactivity of the aldehyde group is known to be considerably diminished, especially when there is a free hydroxyl group in the para position with respect to the aldehyde group.[6] In the course of earlier work, difficulties were experienced on account of the adverse effect of too many free hydroxyl groups in the aldehyde component, and so, either partial benzoylation or benzylation was resorted to in order to prevent failure of the condensation, or to obtain higher yields. For example, in the synthesis of 5-O-methyl pelargonidin,[7] monomethylphloroglucinaldehyde was not directly used for the condensation, but was first converted into its monobenzyl derivative; similarly, hydroxy quinol aldehyde was first benzoylated before being used for pyrylium salt condensation.[8] In the course of the present work, it is found that the pyrylium salt preparation can be carried out successfully with a number of free hydroxyl groups in the aldehyde component without loss of yields.

Hill and Melhuish[9] have reported that 4-phenacyl pyrylium salts are also formed when pyrylium salt condensation is carried out with *p*-methoxy acetophenone in ether solution and that this does not happen in acetic acid medium. In the course of the experiments, described in this paper, it is found that *p*-methoxy acetophenone requires a higher temperature (30°) for its successful condensation, and hence ether could not be used as solvent; glacial acetic acid gives good results. Further, this solvent prevents the formation of phenacyl pyrylium salts.

Experimental

6: 4′-*Dihydroxy flavylium chloride*

It was prepared earlier by Ridgway and Robinson[3] by demethylating the product of condensation of 2-hydroxy-5-methoxy benzaldehyde with *p*-methoxy acetophenone. It has now been made directly from gentisic aldehyde.

Gentisic aldehyde (0·8 g.) obtained by the nuclear oxidation of salicylaldehyde was dissolved in dry ethyl acetate (80 c.c.), *p*-hydroxy acetophenone (1·1 g.) added, and the mixture cooled to 10° and saturated with dry hydrogen chloride. After keeping for 48 hours, excess of ether was added, and the brown red crystals of the pyrylium chloride (1 g.) were collected, and recrystallised from 5% hydrochloric acid when reddish brown glistening plates were obtained (Found: C, 61·2; H, 4·8; Cl, 11·3. $C_{15}H_{11}O_3Cl$, H_2O requires C, 61·5; H, 4·4; Cl, 12·1%). It decomposes at 240–41°, gives a brilliant bluish red colour with aqueous sodium carbonate, a purple colour with sodium hydroxide, and a marked green fluorescence in concentrated sulphuric acid; it is highly stable in the oxidation test and its extraction by the cyanidin reagent is poor.

6-Hydroxy-4′-methoxy flavylium chloride

Gentisic aldehyde (0·6 g.) and *p*-methoxy acetophenone (1·2 g.) were dissolved in glacial acetic acid (50 c.c.) and saturated with dry hydrogen chloride at room temperature (30°). The reaction mixture was allowed to stand for 48 hours, excess of ether added, and the precipitated pyrylium salt (0·9 g.) filtered, washed with ether, and recrystallised from 5% hydrochloric acid, when fine wedge-shaped purplish red crystals were obtained (Found: C, 60·9; H, 4·9. $C_{16}H_{13}O_3Cl$, 1·5 H_2O requires C, 60·9; H, 5·1%. Found in a sample dried *in vacuo* for 7 hours: C, 66·7; H, 4·8. $C_{16}H_{13}O_3Cl$ requires C, 66·6; H, 4·5%).

It decomposes between 143° and 146°, gives with aqueous sodium carbonate a crimson colour which becomes wine red on the addition of sodium hydroxide, exhibits a strong green fluorescence in concentrated sulphuric acid; is highly stable in the oxidation test, and forms no colour base. Its extractability by the cyanidin reagent is very poor.

6: 4′-*Dihydroxy-8-methoxy flavylium chloride*

2: 5-Dihydroxy-3-methoxy benzaldehyde (0·5 g.) obtained by the nuclear oxidation of *o*-vanillin and *p*-hydroxy acetophenone (0·8 g.) were dissolved in dry ethyl acetate (100 c.c.), cooled to 5°, and saturated with dry hydrogen chloride. The mixture was allowed to stand for two days at room temperature, excess of ether added, and the pyrylium salt that had separated out (1 g.) was filtered and recrystallised from 5% hydrochloric acid, when brick red tiny prisms were obtained (Found: C, 56·0; H, 5·2. $C_{16}H_{13}O_4Cl$, $2H_2O$ requires C, 56·4; H, 5·0%). It gives a deep bluish red colour in aqueous sodium carbonate, a purple colour in aqueous sodium hydroxide and an extremely weak green fluorescence in concentrated

sulphuric acid. It forms a colour base, is stable in the oxidation test and is not extracted by the cyanidin reagent.

2:4:5-*Trihydroxy benzaldehyde* (*IV*)

β-Resorcylaldehyde (13·8 g.) was dissolved in aqueous sodium hydroxide (10%, 200 c.c.) and the solution cooled to 10°. A solution of potassium persulphate (27·2 g. in 500 c.c. of water) was slowly introduced into it in the course of 4 hours with continuous stirring, the temperature being kept always below 20°. After allowing to stand for 24 hours, the solution was made neutral with dilute hydrochloric acid, and then extracted with ether to remove the unchanged aldehyde (6 g.); sodium sulphite (10 g.) and concentrated hydrochloric acid (120 c.c.) were then added to the aqueous solution, and it was heated in a water-bath at 80° for 20 minutes. The solution was cooled and repeatedly extracted with ether. The ether extract was dried over anhydrous sodium sulphate and finally distilled to remove ether. Hydroxy-quinol aldehyde (1·2 g.) separated out in the form of colourless rectangular plates (m.p. 220°) which turned brown on exposure to air.

6:7:4′-*Trihydroxy flavylium chloride*

Hydroxy-quinol aldehyde (1·5 g.) and *p*-hydroxy acetophenone (1·15 g.) were dissolved in dry ether (300 c.c.) and the solution saturated with dry hydrogen chloride at 0°. The reaction mixture was left in the ice-chest for a day, fresh ether added, and the dark red crystals of the pyrylium chloride (2·5 g.) which separated out were filtered, washed with ether, and recrystallised from 5% hydrochloric acid, when orange red aggregates of needles of the pyrylium chloride were obtained (Found: C, 59·0; H, 4·2. $C_{15}H_{11}O_4Cl$, H_2O requires C, 58·4; H, 4·2%. Found in a sample dried *in vacuo* for 14 hours: C, 62·2; H, 4·3. $C_{15}H_{11}O_4Cl$ requires C, 62·0; H, 3·8%). It darkens at 210° and decomposes between 246° and 248°, gives a purple colour with aqueous sodium carbonate, a green fluorescence in alcohol as well as in concentrated sulphuric acid and a dark brown violet colour with ferric chloride in alcoholic solution and forms a red colour base. Its extractability by the cyanidin reagent is rather poor.

6:7-*Dihydroxy*-4′-*methoxy flavylium chloride*

Hydroxy quinol aldehyde (1·0 g.) and *p*-methoxy acetophenone (1·7 g.) were dissolved in glacial acetic acid (110 c.c.) and saturated with dry hydrogen chloride at room temperature (30°). After two days, excess of ether was added, when a maroon red crystalline solid (2 g.) separated out. It was recrystallised from dilute hydrochloric acid (5%), when reddish brown

rectangular prisms were obtained (Found: C, 58·2; H, 5·3; Cl, 9·1 $C_{16}H_{13}O_4Cl$, 1·5 H_2O requires C, 57·9; H, 4·8; Cl, 10·7%. Found in a sample dried *in vacuo* for 5 hours: C, 63·2; H, 4·4. $C_{16}H_{13}O_4Cl$ requires C, 63·1; H, 4·3%). It darkens at 190°, partly fuses at 224° and decomposes at 241°. It gives a pinkish orange colour with aqueous sodium carbonate, a strong green fluorescence in concentrated sulphuric acid and a dark purple colour with ferric chloride, forms a colour base, is fairly stable in the oxidation test and is largely extracted by the cyanidin reagent.

2: 5-*Dihydroxy*-4: 6-*dimethoxy benzaldehyde* (*V*)

4: 6-Dimethyl phloroglucinaldehyde (10 g.) (m.p. 78°) was dissooved in aqueous sodium hydroxide (10%, 110 c.c.) and the solution cooled to 10°. Potassium persulphate (16·5 g. in 300 c.c. of water) was gradually introduced over a period of 4 hours with continuous stirring. When worked up as already described for a similar case, 2: 5-dihydroxy-4: 6-dimethoxy benzaldehyde (0·9 g.) melting at 136° was obtained. It was identical with a sample prepared from 2: 6-dimethoxy quinol through the Gattermann reaction and the mixed melting point was undepressed.

5: 7-*Dimethoxy*-6: 4′-*dihydroxy flavylium chloride*

2: 5-Dihydroxy-4: 6-dimethoxy benzaldehyde (0·9 g.) and *p*-hydroxy acetophenone (1·1 g.) were dissolved in dry ethyl acetate (100 c.c.) and the solution saturated with dry hydrogen chloride at 10°. After two days, the dark red product (0·7 g.) was filtered, washed with ethyl acetate, and recrystallised from dilute hydrochloric acid (5%) when brick red rhombic prisms were obtained (Found: C, 54·3; H, 4·4. $C_{17}H_{15}O_5Cl$, H_2O requires C, 54·9; H, 4·8%). It gives a red violet colour with aqueous sodium carbonate, exhibits a feeble green fluorescence in concentrated sulphuric acid and is fairly stable in the oxidation test; its extractability by the cyanidin reagent is very poor.

5: 7: 4′-*Trimethoxy*-6-*hydroxy flavylium chloride*

2: 5-Dihydroxy-4: 6-dimethoxy benzaldehyde (0·2 g.) and *p*-methoxy acetophenone (0·19 g.) were dissolved in glacial acetic acid (75 c.c.) and saturated with dry hydrogen chloride at 30°. After keeping for two days at room temperature, excess of ether was added and the solid that had separated was filtered, washed with ether, and recrystallised from dilute hydrochloric acid (5%), when purplish red long rectangular prisms (0·1 g.) were obtained (Found: C, 55·9; H, 5·9. $C_{18}H_{17}O_5Cl$, $2H_2O$ requires C, 56·1; H, 5·5%). It darkens at 160° and melts with decomposition at 184°, gives a very feeble green fluorescence in concentrated sulphuric acid and an

orange colour with aqueous sodium carbonate which becomes deep red on the addition of sodium hydroxide, does not form a colour base and is highly stable in the oxidation test; its extractability by the cyanidin reagent is very poor.

SUMMARY

Polyhydroxy benzadehydes are prepared by nuclear oxidation of *o*-hydroxy benzaldehyde derivatives with alkaline persulphate and condensed with *p*-hydroxy and *p*-methoxy acetophenones to yield 6-hydroxy pyrylium salts.

REFERENCES

1. Pratt and Robinson .. *J.C.S.*, 1927, 1975.
2. Chapman, Perkin and Robinson .. *Ibid.*, 1927, 3019.
3. Ridgway and Robinson .. *Ibid.*, 1924, 216.
4. Neubauer and Aureli .. *Z. Physiol. Chem.*, 1907, **52**, 375.
5. Baker, Brown and Scott .. *J.C.S.*, 1939, 1922.
6. Pauly and Buttlar .. *Annalen*, 1911, **383**, 230.
7. Leon, Robertson, Robinson and Seshadri .. *J.C.S.*, 1931, 2672.
8. Healey and Robinson .. *Ibid.*, 1934, 1626.
9. Hill and Melhuish .. *Ibid.*, 1935, 85.

DIPOLE MOMENTS OF CAMPHOR COMPOUNDS*—PART I

By P. T. Narasimhan§

(Department of Chemistry, Madras Christian College, Tambaram, South India)

Received November 25, 1952

(Communicated by Dr. S. V. Anantakrishnan, F.A.SC.)

1. Introduction

From a consideration of the Bredt graphic formula for camphor one might expect that apart from the optical isomers, there are also *cis-trans* isomers due to the puckered six-membered ring. The X-ray investigation of *d*-α, Br, Cl and CN camphors carried out by Wiebenga and Krom (1946) points out to the " boat shape " of the six-membered ring of camphor. Measurements of the dipole moments of some camphor compounds were carried out in order to supplement the study of the structure of the camphor ring. In this paper the dipole moments of camphorquinone, camphor oxime and *iso*-nitroso camphor have been reported and discussed in the light of the X-ray structure of camphor.

2. Experimental

Materials.—Benzene ' Analar ' was repeatedly shaken with concentrated sulphuric acid, washed with water, dried over calcium chloride and then over sodium wire. After fractionation, the middle portion was frozen out and finally stored over sodium wire which retained its metallic lustre. B.Pt. = 80·5° (759 mm.); $d_4^{35} = 0{\cdot}86278$; $n_D^{35} = 1{\cdot}4910$.

d-Camphorquinone (B.D.H.) and *d*-camphor oxime (B.D.H.) were crystallized several times from absolute ethyl alcohol [M.Pt. (uncorr.) 199° and 118° respectively]. *iso*-Nitroso camphor (anti) was prepared according to Forster's (1904) method. M.Pt. (uncorr.) 152·5°.

Apparatus.—For the measurement of dielectric constants a heterodyne beat apparatus similar to the one described by Hudson and Hobbs (1942) was used with the following modifications. The 1000 kc./sec. oscillator employed in the present apparatus was operated with a type 6V6 tube and the plate supply for the tubes was obtained from an electronic

* Based on thesis submitted in August 1950 and accepted for the Degree of Master of Science of the University of Madras.

§ Present Address: Department of Physics, Indian Institute of Science, Bangalore-3.

voltage regulator using type 6J7 and type 2A3 tubes. A valve maintained tuning fork was employed for reference and the whole apparatus electrically shielded and maintained at a uniform temperature. The dielectric cell used was of the Sayce-Briscoe type.

3. RESULTS

The mathematical extrapolation method of Hedestrand (1929) was employed for the computation of dipole moments from the dielectric constant and density data of dilute solutions. The contribution due to atom polarisation was taken to be 5% of the molar refraction (MR_D). Tables I to III summarize the results obtained. All measurements were made at a temperature of 35° C. $\pm$ 0·02.

TABLE I

d-*Camphorquinone in Benzene*

No.	Mole fraction $f_1 \times 10^6$	Dielectric constant ϵ	Density d	$\alpha\epsilon_2$	β
1	0	2·2535	0·86278	..	..
2	3,065	2·3433	0·86376	29·30	0·375
3	4,513	2·3823	0·86431	28·54	0·398
4	5,933	2·4363	0·86488	30·82	0·415
5	8,428	2·5172	0·86578	31·29	0·417
6	10,882	2·5754	0·86674	29·58	0·427

Total polarisation ${}_TP_\infty$ = 505·5 c.c. 1·05 MR_D = 49·6 c.c.
Orientation polarisation ${}_0P$ = 455·9 c.c. μ = 4·78 D

TABLE II

d-*Camphor Oxime in Benzene*

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2·2535	0·86278	..	..
2	8,502	2·2698	0·86541	1·917	0·309
3	10,698	2·2712	0·86600	1·655	0·301
4	14,453	2·2801	0·86715	1·841	0·302
5	16,665	2·2844	0·86780	1·854	0·301
6	23,208	2·2928	0·86963	1·693	0·295

${}_TP_\infty$ = 76·71 c.c. 1·05 MR_D = 49·74 c.c. ${}_0P$ = 26·97 c.c. μ = 1·16 D.

TABLE III

iso-*Nitroso Camphor in Benzene*

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2·2535	0·86278	..	..
2	8,772	2·3860	0·86670	15·105	0·518
3	10,298	2·4104	0·86768	15·236	0·552
4	13,378	2·4601	0·86906	15·443	0·544
5	16,202	2·5001	0·87022	15·220	0·532
6	18,401	2·5371	0·87100	15·412	0·518

$_TP_\infty$ = 280·20 c.c. 1·05 MR_D = 49·52 c.c. $_0P$ = 230·68 c.c. μ = 3·40 D.

4. DISCUSSION

Representing the molecule of camphor with the numbering of carbon atoms as shown in Fig. 1, the atoms 1, 2, 3, 4 and 10 are shown by X-ray analysis to lie in a plane (I) while atoms 6 and 5 with the bonds 1–6, 6–5 and 5-4 lie in another plane (II). Similarly atom 7 and bonds 1–7 and 4–7 constitute the other plane (III). Consequently one may speak of planes II and III as forming a " fork " from the plane I.

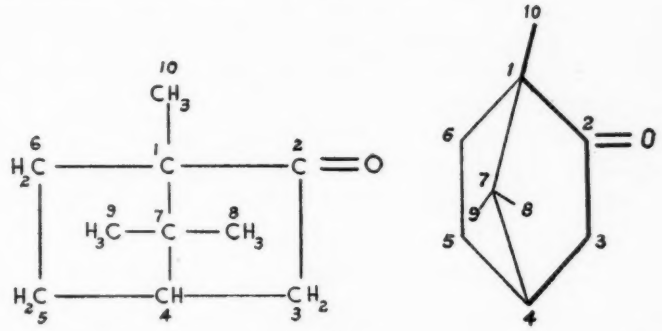


FIG. 1

The total moment of a molecule may be calculated by vectorial addition of the various bond moments. In the case of camphor there is only one strong primary dipole (C = O) as the C—H bond moments may be taken as mutually cancelling each other. This primary dipole will however induce moments of finite magnitude in the neighbouring atoms and groups and account must be taken of such induced moments in calculating the total moment of the molecule. In the present paper the moment contribution

from the planar part (I) of the molecules has been calculated by the method of Groves and Sugden (1937) and the value so obtained compared with the total moment to obtain the moment contribution from the two planes II and III forming the " fork ". Such calculations give a good idea of the general disposition of dipoles with regard to the " fork " in these molecules. Table IV gives the result of calculations carried out for the planar part (I) of camphor according to the method of Groves and Sugden, the notations used here being the same as those used by these authors.

TABLE IV

Induced Moments in Plane I of Camphor

(in terms of $\mu C=O$)

No. of atom or group (see Fig. 1 for notations used)	μ_{ix}	μ_{iy}
1	0·0534	0·1160
3	0·1011	0·2192
4	0·0464	0·0214
10	−0·0750	0·0933

Taking a value of 2·3 D for $\mu C = 0$, the moment contribution from the planar part (I) of camphor is found to be 2·64 D from the appropriate structural diagram while the observed moment of the molecule is 3·0 D (*Tables of Dipole Moments*, 1934).

The moment contribution from the " fork " is therefore 0·36 D. The results of similar calculations carried out for camphorquinone are given in Table V, where the subscripts 1 and 2 refer to the two C = O dipoles.

TABLE V

Induced Moments in Plane I of Camphorquinone

(in terms of $\mu C=O$)

No. of atom or group (see Fig. 1 for notations used)	μ_{ix1}	μ_{ix2}	μ_{iy1}	μ_{iy2}
1	0·0534	0·3192	0·1160	0·3377
4	0·0460	0·0772	0·0210	0·1674
10	−0·0750	0·3441	0·0933	0·4724

The moment contribution from the planar part (I) of this molecule obtained from the appropriate structural diagram is 3·99 D. The observed moment of the molecule being 4·78 D, the contribution due to the " fork " in this molecule is 0·79 D as compared to 0·36 D in the case of camphor. This result suggests a symmetric disposition of the two C = O dipoles with regard to the " fork " in camphorquinone.

Camphor oxime is an interesting case in that chemical resolution of this compound into its two possible isomers has not yet been effected. The dipole moments of the two structures were calculated and the difference was found to be negligibly small. Consequently, the experimentally obtained value will be taken as such in the present discussion. In a preliminary calculation of the moment contribution due to the planar part (I) of this molecule a value of 1·68 D was obtained on the assumption of free rotation of the OH group in = N—OH. The observed moment of the molecule should be greater than this value since the moment contribution from the " fork " has not been added. The moment contribution from the planar part of this molecule in the case of the two extreme structures (A) and (B) represented in Fig. 2 were calculated from the appropriate structural diagrams and found to be 2·67 D and 0·77 D respectively.

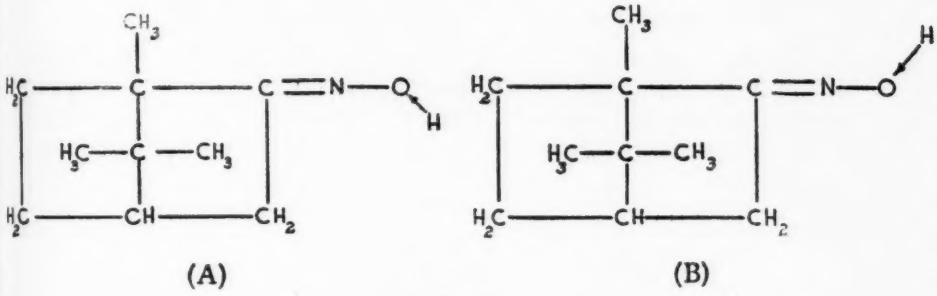


FIG. 2

In accordance with our earlier deduction, the moment contribution due to the " fork " in these structures will be approximately directly proportional to the primary dipole vector and thus the experimental value of 1·16 D seems to favour structure (B) with probably hindered rotation of the OH group. Calculations similar to those given above were carried out in the case of *iso*-nitroso camphor (anti) and a value of 3·14 D was obtained for the moment contribution from the planar part of this molecule on the assumption of free rotation of the OH group. This is in good agreement with the experimental value of 3·4 D obtained for this molecule.

My grateful thanks are due to Dr. S. V. Anantakrishnan for suggesting the problem and for his guidance throughout and to Dr. M. A. Govinda Rao for helpful suggestions and personal discussions on the subject. I thank the University of Madras for a research scholarship which enabled me to carry out a considerable portion of the above work. The Radio Corporation of America has to be thanked for a free gift of two sets of tuning drives to Dr. S. V. A. for use in the equipment. Finally my thanks are due to Prof. A. Viswanathan, formerly of this Department, and to Prof. T. Krishnamoorthy of Presidency College, Madras, for their valuable help.

5. SUMMARY

The dipole moments of camphorquinone, camphor-oxime and *iso*-nitroso camphor have been determined and discussed in the light of the values calculated by the vector addition of bond moments.

REFERENCES

Forster, M. O. .. *J. Chem. Soc.*, 1904, **85 (T)**, 892.
Groves, L. G. and Sugden, S. .. *Ibid.*, 1937, 1992.
Hedestrand, G. .. *Z. phys. Chem.*, 1929, **B2**, 428.
Hudson, B. E. and Hobbs, H. E. .. *Rev. Sci. Inst.*, 1942, **13**, 140.
"Tables of Dipole Moments" .. *Trans. Farad. Soc.*, 1934, **30**, Appendix.
Wiebenga, E. H. and Krom, C. J. .. *Rec. Trav. Chim.*, 1946, **65**, 663.

THIOPHENES AND THIAPYRANS

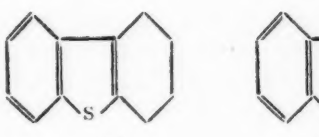
Part IX. Studies in the Dehydrogenation of 1: 2: 3: 4–Tetrahydrodibenzothiophene

By K. Rabindran and B. D. Tilak, F.A.Sc.

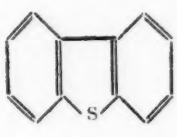
(*Department of Chemical Technology, University of Bombay*)

Received October 1, 1952

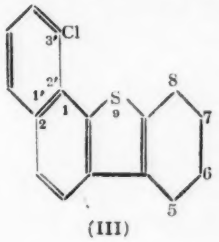
In the new and general synthesis of dibenzothiophene (II) and its derivatives described recently by us, the final step involved dehydrogenation of 1 : 2 : 3 : 4-tetrahydrodibenzothiophene (I) and its derivatives with selenium at 300–20°.[1,2] Although the yield and the purity of the resulting dibenzothiophenes were good in most cases, in a few instances the yield was less satisfactory[2] and in the dehydrogenation of 1 : 2 (3′-chloro-2′ : 1′-benzo)-5 : 6 : 7 : 8-tetrahydro-9-thiafluorene (III) the chlorine atom was eliminated during the dehydrogenation, with the formation of 1 : 2-benzo-9-thiafluorene (IV). In the case of substituted derivatives of (I), there was also the possibility of rearrangement and migration of the substituents during selenium dehydrogenation. Dehydrogenation of the model compound (I) has therefore, been exhaustively studied, with the view to arrive at the optimum conditions whereby the best yield of (II) is obtained under mild experimental conditions. Although dehydrogenation of the hydroaromatic and alicyclic compounds has been widely studied because of its importance in the elucidation of the constitution of natural products, systematic studies in the dehydrogenation of partially and fully reduced heterocyclic compounds, with the



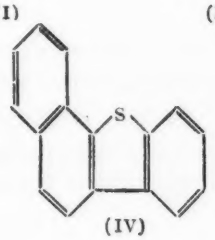
(I)



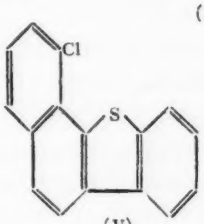
(II)



(III)



(IV)



(V)

possible exception of nitrogen heterocyclics, have not been reported in the literature. The results of the present study are, therefore, of interest not only in the synthesis of thiophene derivatives, but may also be applicable in the dehydrogenation of other heterocyclic compounds.

A brief survey of the different methods of dehydrogenations may be of interest because many of these have been employed in the present work and also because such a consolidated account does not appear to be accessible in the literature. The dehydrogenating agents may be roughly divided into the following four groups:—(1) metal and non-metal reagents, *e.g.*, sulphur and selenium, and platinum, palladium, nickel and copper-chromite catalysts. Whereas sulphur and selenium act by abstracting hydrogen as hydrogen sulphide or hydrogen selenide, the metals act catalytically; (2) quinones which act as hydrogen acceptors by being reduced to the hydroquinone derivatives; (3) halogens which are employed to halogenate the reduced compounds. The desired dehydrogenated product is then obtained by dehydrohalogenation of the intermediate halogeno derivative by treatment with a basic reagent. The intermediate halogeno derivative need not be isolated; (4) oxidizing agents like lead tetra-acetate and selenium dioxide. The first three methods are reviewed and the last method is not discussed as its use in the present work is precluded because of the susceptibility of the sulphur atom in the thiophene derivatives to oxidation.

Dehydrogenation by means of sulphur, selenium, and active forms of platinum and palladium has been discussed in a review by Plattner.[3] By the reaction with Raney nickel, preferably in presence of hydrogen acceptors such as benzene[4] or better cyclohexanone,[5] dehydrogenation of heterocyclic, alicyclic and hydroaromatic compounds have been carried out. When benzene is used as a hydrogen acceptor, the reaction is carried out under pressure at 275–370°, but when cyclohexanone is used, the reaction may be conducted in solvents at 70–150°. Vapour phase dehydrogenation has found commercial application in the dehydrogenation of terpenes, although the reaction may also be carried out in the liquid phase by use of sulphur or a copper-nickel formate catalyst.[6]

Chloranil, which was first introduced as a mild dehydrogenating agent for a few alicyclic and hydroaromatic compounds,[7] has recently been employed for the dehydrogenation of several hydroaromatic compounds such as tetralin which contain the group $-\overset{|}{C}H-\overset{|}{C}H-$ adjacent to the aromatic nucleus.[8] By use of this reagent the dehydrogenation of reduced carbazole derivatives can be effected in good yields.[9]

Iodine and bromine [in the free form or in the form of N-bromosuccinimide (NBS)] have been employed in carrying out dehydrogenations. Iodine has been employed for the conversion of tetralin to naphthalene,[10] flavanones to flavones[10] and recently for the conversion of 1:2:3:4-tetrahydroanthraquinone to anthraquinone.[12] *l*-Menthone can be readily converted to thymol by bromination and subsequent elimination of hydrogen bromide by treatment with quinoline.[6] The Wohl-Ziegler reaction[13] of bromination of olefines and aromatic and ketonic substances by means of NBS has been extended recently for effecting the dehydrogenation of tetralin[14] and of a 2:3-dihydrocoumarone derivative.[15] Dehydrogenation of tetralin is carried out by heating with the calculated quantity of NBS and a small amount of benzoyl peroxide in boiling carbon tetrachloride followed by addition of potassium acetate and acetic acid and continuing heating.[11] The reaction is thus carried out under mild conditions and is complete in one hour. 1:4-Dibromo-1:2:3:4-tetrahydronaphthalene, which is probably formed in the initial step, gives naphthalene by loss of two molecules of hydrogen bromide in the sodium acetate-acetic acid treatment. Whereas dehydrogenation with selenium or palladized carbon is carried out under drastic conditions, dehydrogenation with NBS is carried out under mild conditions, and the method promises to be of general application in compounds other than tetralin.

Most of the important dehydrogenating agents, discussed above, have been employed in the dehydrogenation of (I). The results are summarized in Table (I). Dehydrogenation with NBS was the mildest method employed and promises to be of particular value in the dehydrogenation of substituted derivatives of (I), containing functional groups such as methyl, methoxyl and halogen which are likely to suffer rearrangement or elimination under drastic conditions of dehydrogenation. Thus dehydrogenation of (III) with NBS, gave 1:2 (3′-chloro-2′:1′-benzo)-9-thiafluorene (V), whereas dehydrogenation with selenium gave (IV). When the reaction product in the dehydrogenation of (III) with NBS was heated to remove residual carbon tetrachloride, considerable evolution of hydrogen bromide was noticed. In the dehydrogenation of (I) similar loss of hydrogen bromide was observed during vacuum distillation of the crude reaction product. It appears, therefore, that the dehydrobromination is not complete during the treatment with sodium acetate-acetic acid, but goes to completion during the heating involved in the isolation of the dehydrogenated product.

Dehydrogenation with selenium or palladized carbon, however, gave a clean product in high yield and even the crude substance obtained by solvent extraction was quite pure (m.p. 94–97°). Where the reduced dibenzothiophene

derivative is unlikely to undergo structural change, dehydrogenation by means of selenium or palladized carbon may be the methods of choice. The yield of (II) was slightly better when the dehydrogenation with palladized carbon was carried out in the presence of a very small amount of p-cymene (the reaction temperature remaining the same), than in the absence of a solvent. This may be due to the fact that unreacted (I) is brought into the reaction zone by the boiling solvent, whereas in the absence of a solvent, part of (I) gets mixed up with the sublimed product (II) and is thus removed from the reaction zone.

As regards the efficacy of other dehydrogenation methods employed, the data summarized in Table I is self-explanatory and these methods have no advantage over the use of NBS, selenium or palladized carbon.

Attempts to dehydrogenate (I) by treatment with iodine in boiling alcohol and with Raney nickel in presence of cyclohexanone as hydrogen acceptor were unsuccessful.

EXPERIMENTAL

Reagents employed

1:2:3:4-Tetrahydrodibenzothiophene (I) was prepared according to our recent communication.[1,2]

Dehydrogenating agents

Sulphur:—B.D.H. reagent sublimed.

Selenium powder:—B.D.H. reagent.

Palladized carbon (30%):—Prepared from palladium tetrachloride according to Vogel.[16]

Chloranil:—m.p., 290°.

Iodine:—B.P. Quality.

N-Bromosuccinimide:—Prepared according to Shirley.[17] m.p., 172° (quick heating).

Solvents

Quinoline:—B.D.H. Synthetic.

p-Cymene:— B.D.H. MAR quality.

Nitrobenzene:—B.P. 210–12°.

Carbon tetrachloride:—B.D.H. Redistilled.

Procedure

Dehydrogenation of (I) is fully described in the comprehensive Table I. Dehydrogenation of (I) has been carried out according to the methods given

TABLE I

Dehydrogenation of 1:2:3:4-*tetrahydrodibenzothiophene* (*I*)

No.	Amount of (I) g.	Dehydrogenating agent, g.	Solvent and temperature	Reaction time Hours	Crude dibenzothiophene			Pure dibenzothiophene			Reference
					Isolation method	Yield in g. and per cent.	M.P.	Purification method	Yield in g. and per cent.	M.P.	
1	1·900	S, 0·7	210–220°	10	Ether	2·050	Oil	Fractionation, 140–50°/3 mm.	1·150 63%	95–96°	3
2	1·460	S, 0·52	Quinoline 20 c.c. boiling	2	Addition to dilute HCl and ether-extraction	1·372	Oil	(*a*) Fractionation 120–30°/0·5 mm. (*b*) Above product triturated with *n*-hexane (2 c.c.) and solvent decanted off	0·80 56% 0·48 33·5%	85–90° 93–95°	20
3	1·695	Se, 1·65	280–90°	18	Benzene	1·480 90%	94–96°	Fractionation at 140–50°/1·5 mm.	1·465 88·5%	95–96°	21
4	0·810	Pd-C 0·08	325°	7	Product sublimed during reaction	0·707 89%	93–97°	Fractionation, 145–50°/2 mm.	0·633 80%	94–97°	16
5	1·480	Pd-C 0·15	*p*-cymene (0·8 g.) 320°	13	Ether	1·367 94%	95–96°				22
6	1·210	Chloranil 3·3	*p*-xylene 20 c.c. boiling	36	Dilution with H_2O, extraction with benzene. Wash extract with 10% NaOH, H_2O and remove solvent by steam-distillation	1·290	Oil	(*a*) Fractionation, 135–45°/2 mm. (*b*) Above product sublimed, 98–102°/2 mm.	0·880 74% 0·745 63%	83–85° 91–94°	7
7	1·475	I, 4·1 AcONa, 2·65	$PhNO_2$ 20 c.c. boiling	5	$PhNO_2$ removed by steam-distillation	1·600	Oil	(*a*) Fractionation, 140–50°/2 mm. (*b*) Above product triturated with *n*-hexane (3 c.c.)	0·950 66% 0·450 31·5%	89–93° 93–94°	12
8	1·736	NBS 3·35	CCl_4 50 c.c. boiling	1	See ref. 14	2·670	Oil	Fractionation, 145–50°/1·5 mm.	1·115 65·5%	93–95°	14

in the references listed in the table with only minor alterations. The progress of the dehydrogenation was followed in experiments 4 and 5 by the measurement of hydrogen evolved.

Distillation temperatures refer to bath temperatures.

M.P. of dibenzothiophene cited in literature[21, 23]:—95–96° and 99°.

Apparatus.—Experiment 4 was carried out in the modified sublimation apparatus described by Vogel,[16] experiments 1, 2, 3, 7 were carried out in a R.B. Quickfit flask fitted with an air condenser and in experiments 6 and 8 a reflux condenser was used. Experiment 5 was conducted in an apparatus similar to that described by Linstead,[18] but in the present case a reflux condenser is also employed.

Dehydrogenation of (III) with Selenium

A mixture of (III) (1·2 g.) and selenium (0·81 g.) was heated at 300–20° for 14 hours. After cooling, the reaction mixture was extracted with benzene. Removal of benzene gave a brownish red powder (0·8 g., yield 87%) which on sublimation at 160–80°/3 mm. gave shining colourless plates (0·79 g., yield 77%), m.p. 185–86°, which were halogen-free. The m.p. rose to 186–87° by recrystallization from *n*-hexane (Found: C, 81·7; H, 4·5. $C_{16}H_{10}S$ requires C, 82·1; H, 4·3%). The m.p. of the pure product was not depressed by admixture with a sample of pure (IV), m.p. 184–85°, prepared by a different route.[19]

Dehydrogenation of (III) with NBS

A mixture of (III) (250 mg.), NBS (335 mg.), benzoyl peroxide (10 mg.) and carbon tetrachloride (15 c.c.) was refluxed for 30 minutes. Potassium acetate (3 g.) and glacial acetic acid (1 c.c.) were added and heating continued for another 30 minutes. The reaction mixture was poured into cold dilute aqueous sodium hydroxide and ether extracted. The ether extract was washed, dried and solvent removed. When the residual solvent was being removed, evolution of hydrogen bromide occurred. The product on sublimation at 170–80°/0·8 mm., gave a pale yellow substance (168 mg.) m.p. 135–40°, which on two crystallizations from *n*-hexane-benzene, gave (V) as colourless needles, m.p. 147–8° (Found: C, 71·5; H 3·4. $C_{16}H_9ClS$ requires C, 71·5; H, 3·3%). *sym-Trinitrobenzene derivative* gave orange needles from benzene, m.p. 171–72° (Found: N, 9·4. $C_{22}H_{12}ClN_3O_6S$ requires N, 8·7%).

SUMMARY

The dehydrogenation of 1:2:3:4-tetrahydrodibenzothiophene (I) was studied by using various dehydrogenating agents in order to prepare dibenzothiophene (II) in optimum yield under mild conditions. Dehydrogenation

by means of selenium or palladised carbon gave good yields of (II), but the reaction was carried out at high temperatures (> 275°). By employing N-bromosuccinimide, the dehydrogenation could be carried out in a facile manner at lower temperatures (76°). These results are of value in the synthesis of derivatives of (II). Thus, whereas dehydrogenation of the chlorotetrahydrobenzothiafluorene (III) by treatment with selenium gave the benzothiafluorene (IV) by simultaneous dehydrogenation and dechlorination, dehydrogenation with N-bromosuccinimide gave the chlorine-containing benzothiafluorene (V).

We are indebted to the Council of Scientific and Industrial Research for the award of a Fellowship to one of us (K. R.) and to Dr. T. S. Gore for the microanalyses recorded in this paper.

References

1. Rabindran and Tilak .. *Curr. Sci.*, 1951, **20**, 207.
2. ———— .. *Proc. Ind. Acad. Sci.*, 1952, **36A**, 411.
3. Plattner .. *Newer Methods of Preparative Organic Chemistry* (Interscience), 1948, 21.
4. Adkins and Davis .. *J.A.C.S.*, 1949, **71**, 2955.
5. Badcock and Pausaker .. *J.C.S.*, 1951, 1371.
6. Fieser and Fieser .. *Organic Chemistry* (Heath), 1944, 982 and 635.
7. Arnold and Collins .. *J.A.C.S.*, 1939, **61**, 1407.
8. Dost and Van Nes .. *Rec. Trav. Chim.*, 1951, **70**, 403; cited from *C.A.*, 1952, **46**, 458.
9. Barklay and Campbell .. *J.C.S.*, 1945, 530.
10. Shishido and Nozaki .. *J. Soc. Chem. Ind., (Jap.)*, 1944, **47**, 819; cited from *C.A.*, 1948, **42**, 6351.
11. Narasimhachari and Seshadri .. *Proc. Ind. Acad. Sci.*, 1944, **30A**, 151.
12. Ramanathan and Venkataraman Unpublished work.
13. Djerassi .. *Chem. Reviews*, 1948, **43**, 271.
14. Barnes .. *J.A.C.S.*, 1948, **70**, 145.
15. Geissman *et al.* .. *Ibid.*, 1950, **72**, 4326.
16. Vogel .. *A Textbook of Practical Organic Chemistry*, (Longmans), 1951, 823.
17. Shirley .. *Preparation of Organic Intermediates* (Wiley), 1951, 59.
18. Linstead *et al.* .. *J.C.S.*, 1937, 1153.
19. See following paper.
20. Perkin and Plant .. *J.C.S.*, 1923, 694.
21. Buu Hoi and Cagniant .. *Ber.*, 1943, **76B**, 1269.
22. Linstead and Michaelis .. *J.C.S.*, 1940, 1134.
23. Gilman and Jacoby .. *J.O.C.*, 1938, **3**, 108.

THIOPHENES AND THIAPYRANS

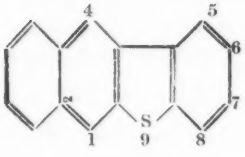
Part X. 1: 2-Benzo-9-thiafluorene and 3:4-Benzo-9-thiafluorene

By K. Rabindran and B. D. Tilak, F.A.Sc.

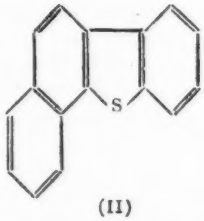
(*Department of Chemical Technology, University of Bombay*)

Received November 27, 1952

Among the three possible benzo-9-thiafluorenes, only the linear isomer 2: 3-benzo-9-thiafluorene (I) is known.[1] The other two isomers 1: 2-benzo-9-thiafluorene (II) and 3: 4-benzo-9-thiafluorene (III) which are angular, have now been synthesized in connection with the study of sulphur isosters of carcinogenic hydrocarbons.[2] Compound (III) is a thiophene analogue of the carcinogenic hydrocarbon, 3: 4-benzphenanthrene. An unsuccessful attempt to synthesize (III) by a modified Pschorr synthesis from phenyl 1-amino-2-naphthyl sulphide has been recently reported.[3] The thiophene derivatives (II) and (III) were prepared by the new dibenzothiophene synthesis described earlier.[4]



(I)

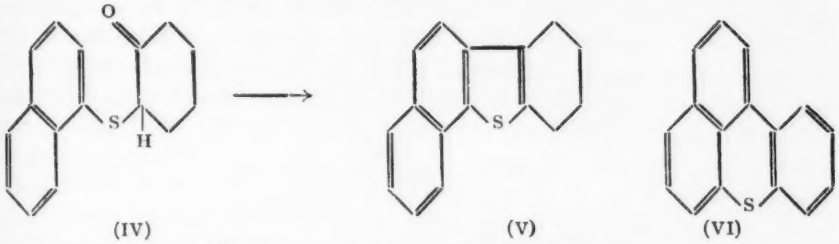


(II)

(III)

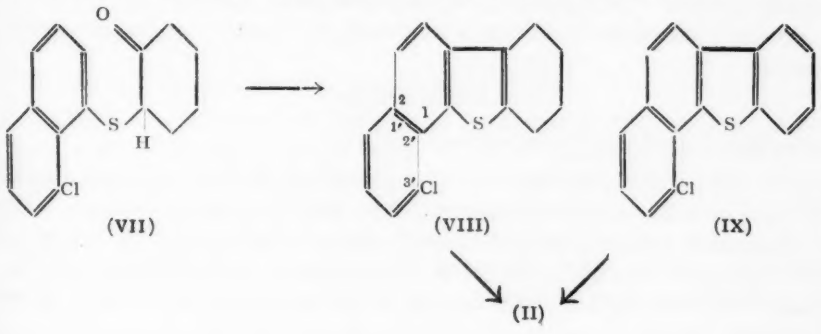
Condensation of α-thionaphthol with 2-bromocyclohexanone gave 2-(α-naphthylmercapto)cyclohexanone (IV) which on cyclization with phosphorus pentoxide gave (A). It was observed that some (A) was also formed during the purification of (IV) by distillation. Dehydrogenation of (A) by selenium gave the compound (B) which may be represented by the two alternative structures (II) or (VI). The former will be formed if the cyclization of (IV) took place in the β-position in naphthalene and the latter if the cyclization took place in the *peri* position. In view of the isosterism between an aromatic double bond and a divalent sulphur atom,[5] the compound (II) is an isoster of chrysene. The similarity between the absorption spectra of (B) and chrysene[6] indicates that (B) is constituted as (II) and the cyclization product (A) is 1: 2-benzo-5: 6: 7: 8-tetrahydro-9-thiafluorene (V).

The identity of (B) with (II) has been proved by the unambiguous synthesis of the latter compound by starting from 8-chloro-1-thionaphthol. Condensation of the latter with 2-bromocyclohexanone gave 2-(8′-chloro-1′-naphthylmercapto)cyclohexanone (VII). Cyclization of the latter can only



(IV) (V) (VI)

take place in the β-position in the naphthalene nucleus, as the *peri* position is blocked by the chlorine atom. Treatment of (VII) with phosphorus pentoxide, therefore, gave 1: 2-(3′-chloro-2′: 1′-benzo)-5: 6: 7: 8-tetrahydro-9-thiafluorene (VIII). As in the case of (IV), distillation of (VII) also resulted in its cyclization, but in this case the ring-closure was complete as the distilled product did not give a 2: 4-dinitrophenylhydrazone. Treatment of (VIII) with selenium[8] gave 1: 2-benzo-9-thiafluorene (II) by simultaneous dehydrogenation and dechlorination.[7] Although the product obtained in this manner proved to be identical with (B), the removal of chlorine during the dehydrogenation which was carried out at 300–20°, left a doubt as regards the constitution of the dehydrogenation product obtained from (VIII). Due to the possibility of structural changes which may accompany dehydrogenation with selenium, it was necessary to dehydrogenate (VIII) in such a way as to retain the chlorine atom in the molecule. This was achieved by effecting the dehydrogenation with N-bromosuccinimide when 1: 2-(3′-chloro-2′: 1′-benzo)-9-thiafluorene (IX) was obtained.[7] Dechlorination of the latter by cuprous acetate in pyridine[9] gave a product which is

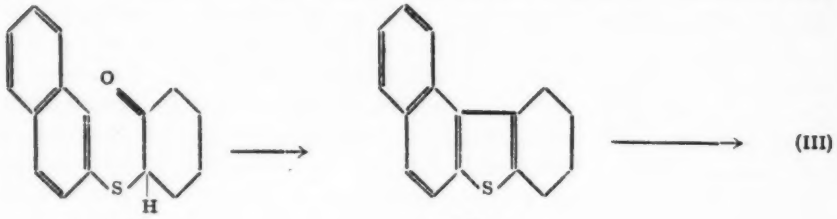


(VII) (VIII) (IX)

(II)

unambiguously constituted as 1:2-benzo-9-thiafluorene (II). This proved to be identical with the product (B) obtained by starting from α-thionaphthol. The constitution of (B) is thus conclusively proved.

β-Thionaphthol on condensation with 2-bromocyclohexanone gave 2-(β-naphthylmercapto)cyclohexanone (X) which could not be isolated as it underwent cyclization during distillation in vacuum. Ring-closure of (X) with phosphorus pentoxide gave a product (C) which was identical with that obtained by the distillation of (X) in vacuum. The cyclization of (X) may take place either in the reactive 1-position or the 3-position in the naphthalene nucleus leading to 3:4-benzo-5:6:7:8-tetrahydro-9-thiafluorene (XI) or to 2:3-benzo-5:6:7:8-tetrahydro-9-thiafluorene respectively. Dehydrogenation of the latter compound will lead to (I), whereas (XI) will give (III). The compound actually obtained by dehydrogenation of (C) was different from (I) and is therefore constituted as 3:4-benzo-9-thiafluorene (III). The cyclization product (C) is thus constituted as (XI).



(X) (XI)

The structures assigned for the benzo-9-thiafluorenes (II) and (III) have been confirmed by Raney nickel desulphurization which led to β-phenylnaphthalene and α-phenylnaphthalene respectively.[10]

Although (III) is isosteric with 3:4-benzphenanthrene, the absorption spectrum of (III) showed greater similarity to chrysene than to 3:4-benzphenanthrene.[6] The similarity of the absorption spectrum of (III) with chrysene rather than 3:4-benzphenanthrene is a matter for further investigation.

EXPERIMENTAL

2-(α-*Naphthylmercapto*)*cyclohexanone* (*IV*)

A mixture of α-thionaphthol (9·2 g.) sodium (1·4 g.), absolute alcohol (50 c.c.) and 2-bromocyclohexanone (11 g.) was refluxed for 6 hours. The condensation product, on isolation by means of ether, gave a brown oil (16·1 g.), most of which distilled at 150–80° (bath temp.)/10 mm. (12·8 g., yield 87%). In further redistillations it was observed that a part of the

product cyclized in each redistillation. The cyclized product distilled at a lower temperature and was separated as an earlier fraction, which gave a picrate but no 2:4-dinitrophenylhydrazone. The higher boiling fraction, which consisted of the condensation product (I) and gave a 2:4-dinitrophenylhydrazone, was a colourless oil, b.p. 215–20°/bath temp./10 mm. (Found: C, 74·3; H, 6·3. $C_{16}H_{16}OS$ requires C, 75·0; H, 6·3%). The 2:4-*dinitrophenylhydrazone* gave orange needles from alcohol-ethyl acetate, m.p. 186–87° (Found: N, 12·5. $C_{22}H_{20}N_4O_4S$ requires N, 12·8%).

1:2-*Benzo*-5:6:7:8-*tetrahydro*-9-*thiafluorene* (*V*)

A mixture of (IV) (4·1 g.) and phosphorus pentoxide (12 g.) was heated at 170–80° for 45 minutes. The reaction mixture was poured into ice water and the oil which separated was isolated by means of ether. The dark coloured oil (3·33 g., yield 88%) on distillation gave a colourless liquid, b.p. 160–80° (bath temp.)/10 mm. (2·7 g., yield 70%), which solidified on cooling. Crystallization from alcohol gave cream coloured needles, m.p. 97–98°. The thiafluorene was finally purified through the picrate and crystallized twice from alcohol when it gave needles, m.p. 97–98° (Found: C, 81·1; H, 6·1. $C_{16}H_{14}S$ requires C, 80·7; H, 5·9%). The *picrate* gave orange needles from alcohol, m.p. 137–38° (Found: N, 8·3. $C_{22}H_{17}N_3O_7S$ requires N, 9·0%).

1:2-*Benzo*-9-*thiafluorene* (*II*)

A mixture of (V) (2·8 g.) and selenium powder (2·16 g.) was heated at 300° for 22 hours. After cooling, the reaction product was extracted with benzene. The brown product (2·46 g., yield 90%) obtained after removal of benzene was twice crystallized from *n*-hexane-benzene when (II) separated as colourless broken plates, m.p. 184–85° (Found: C, 81·9; H, 4·6. $C_{16}H_{10}S$ requires C, 82·1; H, 4·3%). The *sym-trinitrobenzene derivative* gave yellow needles, from benzene, m.p. 176–77° (Found: N, 9·2. $C_{22}H_{13}N_3O_6S$ requires N, 9·4%).

2-(8′-*Chloro*-1′-*naphthylmercapto*)*cyclohexanone* (*VII*)

8-Chloro-1-thionaphthol (10 g.) was dissolved in 30% aqueous sodium hydroxide (6·85 c.c.), cooled in ice-water and 2-bromocyclohexanone (10 g.) was gradually added under vigorous stirring over 10 minutes. The mixture was stirred for one hour and the product isolated by means of ether. Removal of ether gave a dark thick oil (14·8 g., yield 99%), which on distillation gave a yellow liquid, b.p. 180–200° (bath temp.)/1 mm., which solidified on standing. The distillate gave no dinitrophenylhydrazone, but only a picrate showing complete cyclization of the condensed compound.

The 2:4-*dinitrophenylhydrazone* prepared from the crude condensation product (VII) could not be purified.

1:2-(3′-*Chloro*-2′:1′-*benzo*)-5:6:7:8-*tetrahydro*-9-*thiafluorene* (*VIII*)

A mixture of the crude condensation product (VII) (6·3 g.) and phosphorus pentoxide (18 g.) was heated at 160–70° for 45 minutes. The reaction product, isolated in the usual manner, was a dark coloured oil (4·4 g., yield 74%), which soon partly solidified. Distillation of the oil gave a colourless liquid, b.p. 180–200° (bath temp.)/2·5 mm., which solidified on standing. Crystallization of the reaction product (3·92 g., 66%), m.p. 93–95° from alcohol-*n*-hexane gave colourless needles, m.p. 95–95·5° of (VIII) (Found: C, 70·6; H, 5·0. $C_{16}H_{13}ClS$ requires C, 70·4; H, 4·8%). The m.p. of (VIII) was not depressed by admixture with the product obtained by the vacuum distillation of (VII). The *sym-trinitrobenzene derivative* gave yellow needles from benzene, m.p. 154–55° (Found: N, 8·5. $C_{22}H_{16}ClN_3O_6S$ requires N, 8·7%).

The dehydrogenation of (VIII) with selenium and N-bromosuccinimide, which has been described in the previous communication, gave (II) and (IX) respectively.[7]

Synthesis of 1:2-*benzo*-9-*thiafluorene* (*II*) *by the dechlorination of* (*IX*)

A mixture of (IX) (100 mg.), freshly prepared cuprous oxide (54 mg.), acetic anhydride (40 mg.) and pyridine (200 mg.) were heated at 180–200° for 15 hours. The reaction mixture after cooling was added to dilute ammonia and extracted with benzene. The benzene extract was successively washed with dilute hydrochloric acid, dilute sodium hydroxide and water and dried. Removal of benzene gave a yellow brown product (96 mg.), which on sublimation at 160–80°/0·8 mm. gave pale yellow plates (60 mg., yield 69%), m.p. 170°; raised to 184–85° by recrystallization from *n*-hexane. The m.p. of the purified product which was chlorine-free, was not depressed when mixed with (II), m.p. 184–85°, obtained earlier starting from α-thionaphthol.

2-(β-*Naphthylmercapto*)*cyclohexanone* (*X*)

2-Bromocyclohexanone (10·6 g.) was gradually added to an ice-cooled (20°) solution of β-thionaphthol (9·4 g.) in 35% aqueous sodium hydroxide (6·75 c.c.) during 10 minutes under vigorous stirring. After stirring for 1½ hours the mixture was diluted with water and ether extracted. The ether extract after washing successively with alkali and water was dried. Removal of ether gave (IX) as a dark coloured liquid (14·15 g., yield 93%), which

could not be purified as it underwent cyclization during distillation. Thus whereas the crude product gave a 2: 4-dinitrophenylhydrazone, the distilled product gave a picrate but not the hydrazone derivative. The 2: 4-*dinitrophenylhydrazone* from the crude (X) could not be purified by crystallization.

3: 4-*Benzo*-5: 6: 7: 8-*tetrahydro*-9-*thiafluorene* (*XI*)

A mixture of crude (X) (2·85 g.) and phosphorus pentoxide (9 g.) was heated at 170–80° for 30 minutes. Dilution of the reaction mixture with water and ether extraction gave an oil (2·675 g.) which was distilled. The fraction distilling between 190–220° (bath temp.)/5 mm. (1·0 g., yield 38%) solidified on standing and gave colourless needles, m.p. 81·5–82°, of (XI), after crystallization from alcohol (Found: C, 80·3; H, 5·8. $C_{16}H_{14}S$ requires C, 80·7; H, 5·9%).

The cyclization of (X) (1 g.) was also effected by treatment with phosphorus pentoxide (3 g.) in boiling benzene (20 c.c.) for 1 hour. Removal of benzene gave a straw coloured oil (0·764 g., yield 82%), which on dissolution in hot alcohol-*n*-hexane and cooling gave lustrous needles, m.p. 81–82°.

In another experiment crude (X) (3 g.) was distilled and the fraction distilling between 190–230° (bath temp.)/5 mm. (1·2 g., yield 47%) was collected. It solidified on standing and gave, on crystallization from alcohol, a product which was identical with (XI).

The *picrate* from (XI) gave orange needles from alcohol, m.p. 139° (Found: N, 9·2. $C_{22}H_{17}N_3O_7S$ requires N, 9·0%).

3: 4-*Benzo*-9-*thiafluorene* (III)

A mixture of (XI) (1 g.) and selenium (0·75 g.) was heated at 300–20° for 14 hours. The brown product (0·98 g., yield quantitative) obtained by extraction with benzene crystallized from alcohol in elongated colourless needles, m.p. 102–102·5° (Found: C, 81·7; H, 4·6. $C_{16}H_{10}S$ requires C, 82·1; H, 4·3%). The *picrate* gave orange needles from alcohol, m.p. 147–48° (Found: N, 9·0. $C_{22}H_{13}N_3O_7S$ requires N, 9·4%).

The dehydrogenation of (XI) was also effected under milder conditions using *N*-bromosuccinimide. A mixture of (XI) (250 mg.) *N*-bromosuccinimide (375 g.), benzoyl peroxide (10 mg.) and carbon tetrachloride (15 c.c.) was refluxed for 30 minutes. Potassium acetate (3 g.) and glacial acetic acid (1 c.c.) were added and boiling continued for 30 minutes more. After dilution in aqueous alkali, the mixture was extracted with ether. Removal of the solvents gave a dark coloured oil which fumed in air due to evolution

of hydrogen bromide. The product was sublimed at 150°/1 mm. when it gave a crystalline product (160 mg., yield 65%) which, on crystallization from *n*-hexane, gave colourless needles, m.p. 100°, undepressed when mixed with (III) described above.

SUMMARY

The hitherto unknown angular benzo-9-thiafluorenes, 1:2-benzo-9-thiafluorene (II) and 3:4-benzo-9-thiafluorene (III) have been synthesized. The former was prepared starting from α-thionaphthol and 2-bromocyclohexanone. Condensation of these compounds gave 2-(α-naphthylmercapto) cyclohexanone (IV) which on cyclization and dehydrogenation gave (II). The constitution of (II) was proved by its unambiguous synthesis starting from 8-chloro-1-thionaphthol and 2-bromocyclohexanone. Starting from β-thionaphthol, (III) was prepared by similar steps. The constitution of (III) followed from its non-identity with 2:3-benzo-9-thiafluorene.

We are indebted to the Council of Scientific and Industrial Research for the award of a Fellowship to one of us (K.R.), to Dr. M. R. Padhye and Mr. S. R. Desai for the determination of the absorption spectra, to Mr. G. N. Kao for the desulphurization studies and to Dr. T. S. Gore for the microanalyses recorded in this paper.

REFERENCES

1. Mayer .. *Ann.*, 1931, **488**, 259.
2. Tilak *et al.* .. *Proc. Ind. Acad. Sci.*, 1951, **33A**, 131; 1953, **37A**, 114.
3. Neumoyer and Amstutz .. *J.A.C.S.*, 1944, **66**, 1680.
4. Rabindran and Tilak .. *Curr. Sci.*, 1951, **20**, 207; *Proc. Ind. Acad. Sci.*, 1952, **36A**, 411.
5. Bradlow *et al.* .. *J. Chem. Ed.*, 1947, **24**, 433.
6. Desai and Padhye .. Unpublished work.
7. Rabindran and Tilak .. *Proc. Ind. Acad. Sci.*, 1953, **37A**, 557.
8. Plattner .. *Newer Methods of Preparative Organic Chemistry*, (Interscience), 1948, 21.
9. Edwards and Stewart .. *Chem. and Ind.*, 1952, **21**, 472.
10. Kao .. Unpublished work.

THE INFRA-RED ABSORPTION SPECTRUM OF SILICON CARBIDE

By A. K. Ramdas

(From the Raman Research Institute, Bangalore)

Received April 10, 1953

(Communicated by Sir C. V. Raman, F.R.S., N.L.)

1. Introduction

The earliest investigation of the infra-red behaviour of silicon carbide (carborundum) was carried out by Coblentz[1] who studied the reflexion spectrum in the range $1\,\mu$ to $15\,\mu$ using a large hexagonal plate with natural polish. The remarkably strong reflexion maximum at $12\,\mu$ is the most notable feature of this work. Coblentz also studied the transmission of silicon carbide, but the specimen was opaque beyond $4\,\mu$.

Schæfer and Thomas[2] also studied the reflexion and transmission of silicon carbide between $1\,\mu$ and $15\,\mu$. Their reflexion studies confirm Coblentz's results. Using a very clear uniaxial plate of thickness 0·48 mm., they were able to investigate the transmission spectrum upto $7\,\mu$. They observed an absorption maximum at $6{\cdot}24\,\mu$.

In the present paper it is proposed to present the experimental results of the study of the transmission spectra of twelve specimens of silicon carbide from $1\,\mu$ to $20\,\mu$ and discuss them in the light of the X-ray structure determinations.

2. Experimental Results

A Beckman infra-red spectro-photometer (model IR2), provided with potassium bromide optics, was used, the % transmission being read off directly with the instrument. All the specimens are uniaxial and they were studied with their basal plane perpendicular to the infra-red radiation.

Silicon carbide is highly refracting ($\omega = 2{\cdot}65$, $\epsilon = 2{\cdot}69$). The incident radiation is, therefore, completely deflected if the plates are not plane parallel. Thus a false absorption is recorded. Out of the twelve specimens examined, three suffered from this defect and did not, therefore, give any useful results. In Figs. 1 to 4 the % cut-off with wavelength are exhibited for specimens I, IX, III and VI respectively.

Fig. 1 (Specimen I: thickness 0·14 mm.; transparent and colourless). The % cut-off increases from 60% at 1 μ to 97% at 6·3 μ. There are inflexions in between at 3·5 μ, and at 5 μ. There is a well-defined absorption maximum between 6·3 μ and 6·5 μ. Absorption maxima are also clearly noticed at 7·2 μ and 7·7 μ. The region between 9 μ to 14 μ is a region of almost total absorption. Beyond 14 μ the absorption falls off slowly from 100% to 90%. There are some indications of absorption maxima in this region.

Fig. 2 (Specimen IX: thickness 1 mm.; transparent, slight brown tinge. This shows a general similarity with Fig. 1. But there are absorption maxima at 3·2 μ, 4·5 μ and 5 μ quite easily recognisable. In addition, there are maxima at 6·1 μ, 6·4 μ and 7·3 μ. The region between 9 μ to 15 μ is of almost total absorption. Beyond 15 μ the absorption falls off slowly; the fall is even slower than that noticed in Fig. 1.

Fig. 3 (Specimen VI: thickness = 0·5 mm.; transparent, colourless).

This specimen, besides showing maxima between 6·0 μ and 6·5 μ, and at 7·3 μ, has absorption maxima at 3·2 μ and 5·0 μ. The range between 9·0 μ to 12 μ is one of the intense absorption, after which the absorption falls off very rapidly indeed. In this region there are definite signs of further absorption bands.

Fig. 4 (Specimen III: thickness 0·25 mm., transparent, colourless).

This specimen exhibits inflexions at 3·2 μ, 5·0 μ; well-defined absorption maxima at 6·3 μ, and 7·8 μ; and a region of intense absorption maxima between 10 μ and 13 μ beyond which as in the case of specimen IV, Fig. 3, it shows a rapid fall.

Specimen VIII (curve not reproduced), which is coloured green, is remarkable in that it gives a high transmission (50%) upto 3·0 μ and shows intense and uniform absorption beyond that. Specimens VII and X also behave similarly. All these crystals are green coloured and the above behaviour is presumably due to the colour. Specimen XI (curve not reproduced), shows 50% absorption at 1 μ and gradually goes upto 95% at 6·5 μ where there is a definite absorption band. Beyond 9 μ it shows constant and continuous absorption and falls off slowly beyond 14 μ.

3. Crystal Structure of Silicon Carbide

Recent work[3] on the X-ray structure of silicon carbide has revealed the existence of numerous modifications. Ramsdell and Kohn list fourteen different silicon carbide structures, *viz.*, one cubic (T_d^2), three hexagonal (C_{6v}^4) and ten rhombohedral (C_{3v}^5, C_{3v}^1).

Fig. 1.

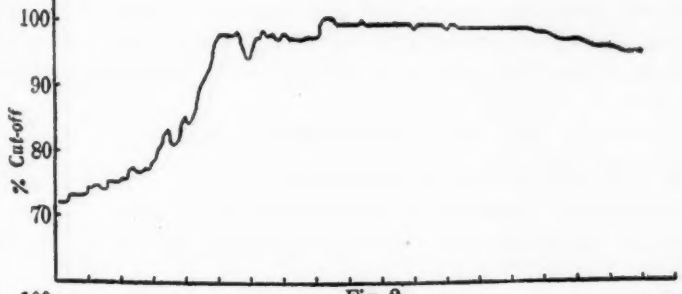


Fig. 2.

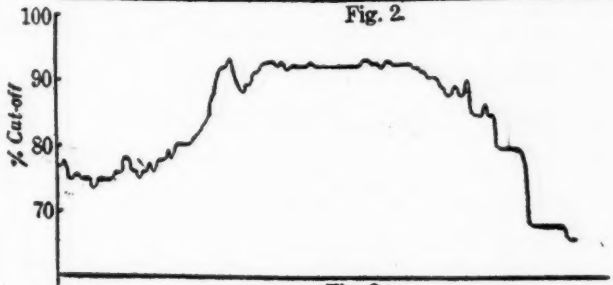


Fig. 3.

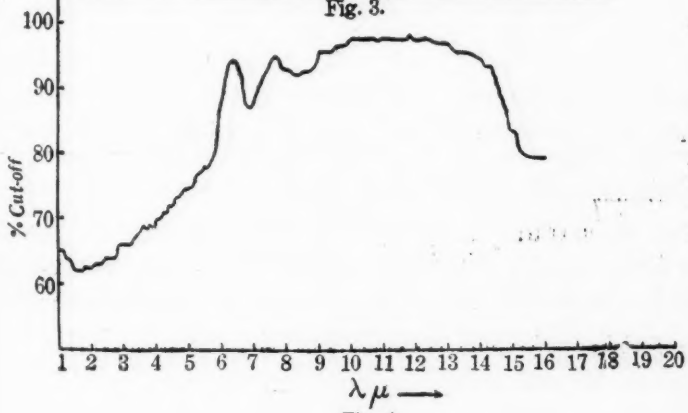


Fig. 4.

FIGS. 1-4. Infra-red absorption spectrum of silicon carbide
(Fig. 1 = Specimen I. Fig. 2 = Specimen IX. Fig. 3 = Specimen VI. Fig. 4 = Specimen III)

The crystal forms of silicon carbide, though formally complex, are simple in basic principle. All of them exhibit tetrahedral structure, *i.e.*, each carbon is bound tetrahedrally to four silicons and each silicon to four carbons. The different forms of silicon carbide can be viewed as centres of tetrahedra stacked one above the other in different sheets, the trigonal axis being perpendicular to these sheets. The several structures then differ in the ways in which these tetrahedra are turned with respect to each other.

In the present case as well as in the previous work, the type to which the different specimens belong has not been ascertained. The only fact known is that all of them are uniaxial. But the close relationship between the different forms enables one to interpret the vibration spectrum in a general way.

4. GROUP THEORETICAL ANALYSIS

If the space group and the position and number of atoms in the unit cell are known, the number of normal modes, their symmetry types, and the selection rules governing their infra-red and Raman activity can be deduced from group theoretical analysis.

We shall now apply group analysis to some of the simpler structures.

(i) Type IV, Cubic – SiC – T_d^2.

The unit cell contains two non-equivalent atoms per unit cell [one Si (1) and one C (2)].

T_d^2	E	8 C_3	3 C_2	6σ_d	6 S_4	n_i	T	n_i'	R	I.R.
A_1 ..	1	1	1	1	1	0	0	0	–	–
A_2 ..	1	1	1	−1	−1	0	0	0	–	–
E ..	2	−1	2	0	0	0	0	0	–	–
F_2 ..	3	0	−1	1	−1	2	1	1	*a*	*a*
F_1 ..	3	0	−1	−1	1	0	0	0	–	–
U_R ..	2	2	2	2	2					

Thus this structure is capable of a triply degenerate vibration, active both in Raman effect and infra-red. In vibration the silicons vibrate against carbons in any arbitrary direction. The normal co-ordinates are:

$Q_a = m_{si}x_2 - m_c x_1$ and similarly Q_b, and Q_c.

(ii) Type III, 4H, Hexagonal: C_{6v}^4, four SiC per unit cell.

(1 to 4 silicons, 5 to 8 carbons)

C_{6v}^4	E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$	n_i	T	n_i'	R	I.R.
A_1 ..	1	1	1	1	1	1	4	1	3	*a*	*a*
A_2 ..	1	1	1	1	−1	−1	0	0	0	–	–
B_2 ..	1	−1	1	−1	1	−1	0	0	0	–	–
B_1 ..	1	−1	1	−1	−1	1	4	0	4	*ia*	*ia*
E_2 ..	2	2	−1	−1	0	0	4	0	4	*a*	*ia*
E_1 ..	2	−2	−1	1	0	0	4	1	3	*a*	*a*
U_R ..	8	0	8	0	0	8					

The form of the normal co-ordinates is:

$$\underline{A_1} \rightarrow Q_i = c_1(z_1 + z_2) + c_2(z_3 + z_4) + c_3(z_5 + z_6) + c_4(z_7 + z_8)$$
$$(i = 1, 2, 3, \text{or } 4)$$

As one translation belongs to this class, one of the normal co-ordinates is:

$$T_z = z_1 + z_2 + z_3 + z_4 + z_5 + z_6 + z_7 + z_8.$$

$$\underline{B_1} \rightarrow Q_i = c_1(z_1 - z_2) + c_2(z_3 - z_4) + c_3(z_5 - z_6) + c_4(z_7 - z_8).$$

$$\underline{E_1} \rightarrow Q_{ia} = a_1(x_1 + x_2) + a_2(x_3 + x_4) + a_3(x_5 + x_3) + a_4(x_7 + x_8)$$

and similarly Q_{ib}. Of these

$$Tx = x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8$$

$$Ty = y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8.$$

$$\underline{E_2} \rightarrow Q_{ia} = b_1(y_1 - y_2) + b_2(y_3 - y_4) + b_3(y_5 - y_6) + b_4(y_7 - y_8)$$

and similarly Q_{ib}.

For the type-6H also one may similarly apply the same method. The number of normal modes in this type naturally increases for each symmetry class, though the general nature of the movements is the same. We thus find that in the hexagonal types of silicon carbide the movements of the atoms are either along the trigonal axis or perpendicular to it.

(iii) Type I, 15 R — SiC. Rhombohedral.—C_{3v}^5.

Five SiC per unit cell (1 to 5 Si; 6 to 10 C).

C_{3v}^5	E	$2C_3$	$3\sigma_v$	n_i	T	n_i'	R	I.R.
A_1 ..	1	1	1	10	1	9	a	a
A_2 ..	1	1	−1	0	0	0	ia	ia
E ..	2	−1	0	10	1	9	a	a
U_R ..	10	10	10					

The form of the normal co-ordinates is:

$$A_1 \rightarrow Q_i = \sum_1^{10} c_i z_i, \quad T_z = \sum_1^{10} z_i$$

$$E \rightarrow Q_{ia} = \sum_1^{10} a_i x_i, \quad T_x = \sum_1^{10} x_i$$

and similarly Q_{ib}.

In this type the oscillations are again confined to the direction along the trigonal axis or perpendicular to it.

5. Interpretation of Observed Facts

From the above analysis it emerges that the normal modes of all the structures of silicon carbide consist of movements of layers perpendicular to the trigonal axis. The movements are either normal to the axis or along it. In the cubic silicon carbide, there is only one normal mode in which silicons oscillate against carbons. In all types of silicon carbide there will be a mode in which silicons and carbons vibrate in opposite phases. This type of oscillation will have the highest frequency and will be active in both infra-red and Raman effect.

The Raman spectrum of specimen IX has been examined by Narayanan.[4] He obtained a line at 818 cm.$^{-1}$ (12·2 μ). The reflexion studies also indicate an extremely intense maximum at 12 μ, while all crystals studied in this investigation show an intense absorption in the range 10 μ to 14 μ. The calculation of the frequency of the only normal mode of the cubic carborundum, making certain assumptions about the force constants (by comparison with the analogous case of diamond), suggests qualitatively that the principal oscillation in which carbons vibrate against silicons, can be ascribed to this 12 μ band, active both in infra-red and Raman effect.

The absorption spectra as well as the group theoretical analysis, however, clearly indicate the existence of numerous other vibrations than the one described above. These will be of lower frequencies and their number will increase with the increasing complexity of the structure. The vibrations

which will be active in infra-red when the crystals are examined in the basal plane, are those in which movements are normal to the optic axis. Even in the simplest type (4H) there are two such vibrations besides the one in which carbons vibrate against silicons. This no doubt accounts for the intense absorption which continues beyond 12μ.

The absorption maxima at $3{\cdot}5\mu$, $5{\cdot}0\mu$; $6{\cdot}3\mu$ to $6{\cdot}5\mu$; and at $7{\cdot}2\mu$ and $7{\cdot}7\mu$ in specimen I; $3{\cdot}2\mu$, $4{\cdot}5\mu$, $5{\cdot}0\mu$, $6{\cdot}1\mu$, $6{\cdot}4\mu$ and $7{\cdot}3\mu$ in specimen IX; $3{\cdot}2\mu$, $5{\cdot}0\mu$; $6{\cdot}0\mu$ to $6{\cdot}5\mu$ in specimen VI; $3{\cdot}2\mu$, $5{\cdot}0\mu$, $6{\cdot}3\mu$ and $7{\cdot}8\mu$ in specimen III—all these can be interpreted as first order and second order combinations and overtones of the fundamentals. This also indicates the existence of fundamentals other than the one at 12μ.

In conclusion, I wish to express my grateful thanks to Professor Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for his encouragement and guidance.

Summary

The absorption spectra of crystals of silicon carbide, studied in the range of 1μ to 20μ, reveal besides an intense region of absorption from 10μ to 14μ in which the reflexion maximum at 12μ falls, several comparatively well-defined absorption maxima at shorter wavelengths, *viz.*, at $3{\cdot}5\mu$, $5{\cdot}0\mu$, $6{\cdot}3\mu$ to $6{\cdot}5\mu$, $7{\cdot}2\mu$ and $7{\cdot}7\mu$ in a typical case.

Silicon carbide exists in various crystal forms. From a group theoretical analysis applied to a few typical cases it emerges that the normal modes of the uniaxial silicon carbide consist of movements of silicons and carbons along the optic axis or normal to it.

The reflexion maximum at 12μ, and the Raman line at 818 cm.$^{-1}$ ($12{\cdot}2\mu$) can be attributed to an oscillation in which carbons and silicons vibrate in opposite phases. The existence of numerous other vibrations besides this one accounts for the extension of the absorption band beyond 12μ. The absorption maxima in the short wavelengths can be attributed to first order and second order combinations and overtones of these fundamentals.

References

1. Coblentz .. *Investigations of Infra-Red Spectra*, Carnegie Institution Publication, 1908, 36 and 42.
2. Schæfer and Thomas .. *Z. für. Physik.*, 1923, **12**, 330.
3. Ramsdell and Kohn .. *Acta. Cryst.*, 1952, **5**, 215.
   Taylor and Laider .. *British Jour. Appl. Phy.*, 1950, **1**, 174.
4. Narayanan .. *Curr. Sci.*, 1952, **21**, 239.

DIPOLE MOMENTS OF TETRAHYDROPYRAN AND DIHYDROPYRAN*

By Sundaresa Soundararajan§ and S. V. Anantakrishnan, F.A.Sc.

(Department of Chemistry, Madras Christian College, Tambaram)

Received January 2, 1953

Introduction

The dipole moments of heterocyclic compounds are of interest both for an indication of the valency angle of the hetero atom and for information as to the spatial disposition of the members of a ring system. Pyrans have the added interest on account of their relationship with the hexoses. Since Allen and Hibbert[1] reported a value of 1·87 D for the dipole moment of tetrahydropy an, there have been improvements in the design of apparatus used as well as in experimental technique, especially in the design of constant frequency oscillators.[7, 9, 15, 28] Besides, greater accuracy is also possible now in the extrapolation methods for computing ${}_{T}P_{\infty}$ at infinite dilution.[16, 17, 20, 23] It was therefore considered desirable to redetermine the value for tetrahydropyran. The results of measurements on tetrahydropyran and dihydropyran have been recorded here and their structures discussed in the light of the results obtained.

Experimental

Materials.—' AnalaR ' benzene was repeatedly shaken with concentrated sulphuric acid, washed thoroughly with water, treated with a solution of sodium hydroxide, washed again with water and dried over anhydrous calcium chloride. The middle portion obtained by fractional distillation was frozen out. The portion freezing last was rejected and the benzene after melting was stored over pure sodium wire which retained its metallic lustre.

Tetrahydropyran obtained from the I.C.I. was dried over anhydrous sodium sulphate, distilled in an all-glass apparatus and the middle fraction collecting between 87° and 88° was used.

Dihydropyran obtained from the I.C.I. was dried over potassium hydroxide, distilled in an all-glass apparatus and the middle fraction collecting between 86° and 87° was used for the determinations.

---

* Based on thesis of S. S. approved for the M.Sc. degree of Madras University.

§ Present address: Department of General Chemistry, Indian Institute of Science, Bangalore-3.

Apparatus.—Dielectric constant measurements were made with an A.C. mains operated heterodyne beat apparatus similar to that of Hudson and Hobbs[21] with the following modifications. The crystal oscillator employed a hermetically sealed quartz crystal with a frequency of 1,000 kc./sec. and a temperature coefficient of 0·0001% per° C. and an RCA 6V6 valve, operated with a plate voltage of 250 V. The electron coupled critical oscillator with the radio frequency mixer was similar to that of Hudson and Hobbs. Following the radio frequency mixer, a three stage valve amplifier, specially suited to the operation of a pair of low frequency phones was used. An efficient electronic stabiliser circuit[8] following the power supply was used to achieve complete stabilisation of plate potentials. To ensure frequency stability, the whole assembly was enclosed in an aluminium case and was maintained at a constant temperature of 35° C. by means of an air thermostat. Special attention was given to the rigidity of the mountings and shielded cables were used in all R.F. current carrying sections. Radio frequency chokes were employed in the L.T. lines to prevent stray R.F. currents. In the tank circuit of the crystal oscillator, in parallel with a variable air condenser of 0·0005 mfd was a coil of 50 turns of D.S.C. wire No. 20 S.W.G wound on a bakelite former of 3″ diameter with a length to diameter ratio of 1 : 1·37 because this ratio minimised the temperature variation of inductance.[14] In the critical oscillator a similar coil was placed in parallel with the Sayce Briscoe dielectric constant cell of about 50 mmfd capacity and the measuring precision condenser. The measuring condenser had a capacity of about 500 mmfd. Coupled to this were two sets of compact tuning drives consisting of a set of toothed double wheels having interconnected springs to avoid backlash and fitted with a rotating scale disc and a graduated vernier strip. The precision condenser was thus capable of fine adjustments and even small settings could be measured accurately.

The true capacity of the test cell was obtained after calibrating the measuring condenser for linearity as indicated by Smyth[31] and applying corrections for leads[12, 29] and finally for the replaceable capacity by evaluation of the zero capacity C_0.[22] The dielectric constants of the solutions were evaluated from the standard equation

$$\epsilon_s = \frac{C_0 - C_S}{C_0 - C_A}.$$

Densities of the dilute benzene solutions were obtained using an Ostwald Sprengel pycnometer with ground-in caps closing both ends. Refractive indices of solutions of various concentrations were straightway read from an Abbe refractometer. The molar refraction obtained from measurements was compared with that calculated using the additivity of bond refractions.[10]

The polarisation $_TP_\infty$ at infinite dilution of the solute was obtained from the average of the calculated values of Hedestrand constants, α and β given in the following tables.

TABLE I

Tetrahydropyran in Benzene—Temp. 35° ± 0·005° C.

Concentration in mole fractions	Dielectric constant	Density	α	β
0·000000	2·2535	0·86278	..	..
0·004962	2·2732	0·86298	1·772	0·0429
0·012068	2·2927	0·86325	1·404	0·0425
0·018338	2·3115	0·86347	1·407	0·0451
0·037196	2·3714	0·86425	1·370	0·0433
0·073825	2·4848	0·86550	1·441	0·0432

$_MR_D$ measured = 24·2 c.c. $_TP_\infty$ = 78·33

$_MR_B$ calculated = 24·92 c.c. μ = 1·63D

TABLE II

Dihydropyran in Benzene—Temp. 35° ± 0·005° C.

Concentration in mole fractions	Dielectric constant	Density	α	β
0·000000	2·2535	0·86278	..	..
0·026371	2·3165	0·86480	1·060	0·089
0·053563	2·3851	0·86673	1·091	0·085
0·083208	2·4600	0·86881	1·101	0·084
0·099261	2·5009	0·87010	1·101	0·089
0·130717	2·5760	0·87232	1·064	0·089

$_MR_D$ measured = 24·1 c.c. $_TP_\infty$ = 63·09

$_MR_B$ calculated = 24·45 c.c. μ = 1·38D

DISCUSSION

Allen and Hibbert[1] suggested that the six-membered tetra hydropyran ring is diplanar and if this be so then a puckering of the ring will enable the valence bonds to assume any convenient angle so that any strain on these bonds will be very small. Recently DeVries Robles,[11] in discussing the

effect of cyclisation of the ethylene oxide homologues on the electric moments, calculated the strain in each of the molecules from simple energy considerations and assigned to each the most probable structure. According to him the strain is zero for both tetrahydropyran and dioxan, both having a strainless structure, on account of the great freedom of the ring. The molecules can occur both in the stiff chair form and in the mobile form. In the mobile form are a continuous series of crossed structures of which the boat form is a particular position.

The evidence of various physical measurements leaves no doubt that the natural valency angle of oxygen is close to the tetrahedral angle of 109°. Thus an angle of 110° has been obtained in the crystal structure of ice.[2] Pople[27] using the theory of molecular and equivalent orbitals, obtains for the oxygen valency angle an equilibrium value of 105°, both hybridization parameters being close to the value that may be expected for tetrahedral orbitals, originally introduced by Pauling[26] in 1931. Thus the equivalent orbital description of the water molecule assigns it an approximately tetradedral character, with bond orbitals pointing in two of the directions and equivalent lone pairs in the other two. This may be regarded as a theoretical foundation for the tetrahedral model used by Bernal and Fowler.[6] A study of the collision areas of ethers points in the same direction[19] and the infra-red spectrum of water vapour has led to various values ranging from 105° to 110°.[24,25] Bennet[4,5] taking the C–C and C–O distances in dimethyl ether as 1·54 A and 1·40 A respectively and the C–C bond moment as 0·2 D obtained a value of 1·01 D for the C–O bond moment. The moment of dimethyl ether then leads to a valency angle of 115° (see however Gent[13]). Yet an analysis of the dipole moments of some diphenyl ethers indicates that, in these substances, the angle is probably larger than the tetrahedral value and Hampson[18] has calculated a value of 124° to 132° for the oxygen valency angle in these ethers. However, there is no justification for supposing that the valency angle of oxygen in other compounds is necessarily the same as in diphenyl ethers. Sutton and Brockway[30] find 105° ± 5°, 111° ± 2°, 111° ± 4° and 110° ± 5° for the oxygen valence angle in F_2O, Cl_2O, $(CH_3)_2O$ and dioxan respectively.

In the case of tetrahydropyran, using the bond moment values and an oxygen valence angle of 93°, Allen and Hibbert (*loc. cit.*) calculate a dipole moment value agreeing with their experimental value of 1·87 D, while Gent (*loc. cit.*) using their experimental value obtains for the valence angle a value of 111°. This has been obtained using a bond moment of 0·4 D for the C–H bond and 1·15 D for the C–O bond. Allen and Hibbert's calculations for a valence angle of 110° leads to a moment of 1·65 D

a value which conforms to our experimental observations. De Vries Robles (*loc. cit.*) reports for tetrahydropyran a valence angle of 111° while Beach[3] has reported a similar value from experimental results with tetramethylene oxide. Taking all factors into account we may then consider that the valence angle of oxygen in these compounds is about 111°.

In the case of dihydropyran, the introduction of a double bond alters the moment appreciably. The ring system will tend to planarity thus leading to a reduced moment. This is clearly shown by the experimental value of 1·38 D.

One of us (S. S.) thanks Dr. M. A. Govinda Rau for his helpful suggestions and personal discussion and Mr. A. Visvanathan, Mr. P. T. Narasimhan and Prof. T. Krishnamoorti of Presidency College for their valuable help.

The authors thank the Radio Corporation of America for the gift of a precision tuning drive used in the experiments and the Imperial Chemical Industries for a gift of the two compounds used in these studies.

SUMMARY

The dipole moments of tetrahydropyran and dihydropyran have been obtained from measurements of dielectric constants of benzene solutions using a heterodyne beat method and following Hedestrand's method of extrapolation for arriving at the value for total polarisation. The results obtained have been discussed in relation to the structure of these compounds.

REFERENCES

1. Allen and Hibbert, H. .. *J.A.C.S.*, 1934, **56**, 1398.
2. Barnes, W. H. .. *Proc. Roy. Soc.*, 1929, **125 A**, 670.
3. Beach .. *J. Chem. Phys.*, 1940, **9**, 54.
4. Bennett, G. M. .. *Trans. Farad. Soc.*, 1934, **30**, 852.
5. ———, G. M. and Glasstone, S. .. *Proc. Roy. Soc.*, 1934, **145 A**, 71.
6. Bernal, J. D. and Fowler, R. H. .. *J. Chem. Phys.*, 1933, **1**, 515.
7. Bloom, G. I. M. and Sutton, L. E. .. *J.C.S.*, 1941, 727.
8. Chien, J. Y. .. *J. Chem. Educ.*, 1947, **24**, 494.
9. Coop, I. E. and Sutton, L. E. .. *J.C.S.*, 1938, 1269.
10. Denbigh, K. G. .. *Trans. Farad. Soc.*, 1940, **36**, 936.
11. De Vries Robles, H. .. *Rec. Trav. Chim.*, 1940, **59**, 184.
12. Fairbrother, F. .. *Proc. Roy. Soc.*, 1933, **142 A**, 173.
13. Gent, W. L. .. *Quart. Rev.*, 1948, **2**, 387.
14. Griffiths, W. H. F. .. *Exp. Wireless and Wireless Eng.*, 1929, **6**, 543.
15. Groves, L. G. .. *J.C.S.*, 1939, 1144.
16. Guggenheim, E. A. .. *Trans. Farad. Soc.*, 1949, **45**, 714.

17. Halverstadt, I. R. and Kumler, W. D. *J.A.C.S.*, 1942, **64**, 2988.
18. Hampson, G. C. .. *Trans. Farad. Soc.*, 1934, **30**, 859.
19. Hare, W. A. and Mack, E. .. *J.A.C.S.*, 1932, **54**, 4272.
20. Hedestrand, G. .. *Z. Physik. Chem.*, 1928, **2 B**, 428.
21. Hudson, H. and Hobbs, E. .. *Rev. Sci. Instr.*, 1942, **13**, 140.
22. LeFevre, R. J. W. .. *Dipole Moments* (Methuen).
23. ——— and Vine, H. .. *J.C.S.*, 1937, 1805.
24. Leug, P. and Hedfeld, K. .. *Z. Physik.*, 1932, **75**, 512.
25. Mecke, R. .. *Trans. Farad. Soc.*, 1934, **30**, 90.
26. Pauling, L. .. *J.A.C.S.*, 1931, **53**, 1367.
27. Pople, J. A. .. *Proc. Roy. Soc.*, 1950, **202A**, 332.
28. Stranathan, J. D. .. *Rev. Sci. Instr.*, 1934, **5**, 334.
29. Sugden, S. .. *J.C.S.*, 1933, 770.
30. Sutton, L. E. and Brockway, L. O. .. *J.A.C.S.*, 1935, **57**, 473.
31. Smyth, C. P. .. *Weissberger's Physical Methods of Organic Chemistry*, 1949, 1645.

395–53 Printed at The Bangalore Press, Bangalore City, by C. Vasudeva Rao, Superintendent
and Published by The Indian Academy of Sciences, Bangalore

ERRATA

VOL. XXXVII, NO. 2, SECTION 'A'

(1) Page 273, 17th line from the bottom (3rd line of last paragraph) the word " *umbra* " occurring in this line should read as " *penumbra* ";

(2) Plate X, Figure 1. The spelling of the word " sunspot " is incorrect. " *Sonspot* " should read as " *Sunspot* ".